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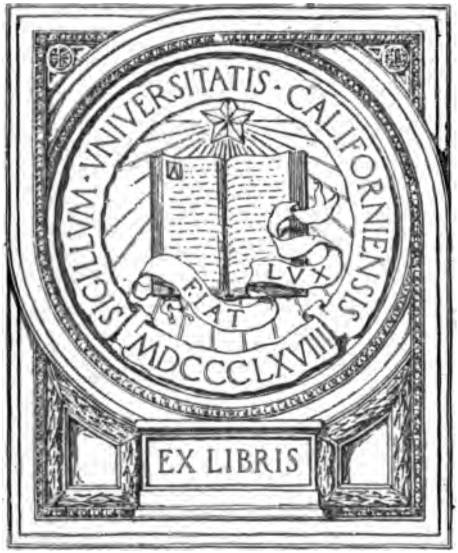

periodic Chart

Chromium [illegible]

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lead

Edward Booth

OUTLINE OF A SHORT COURSE

IN

Qualitative Chemical Analysis

ARRANGED FOR

STUDENTS IN THE COLLEGES OF SCIENCE

OF THE

UNIVERSITY OF CALIFORNIA

BY

W. J. SHARWOOD

INSTRUCTOR IN CHEMISTRY

REVISED EDITION

1898

EDWARD BOOTH

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ERRATA.

Page	16,	line	17,	for	$Ca^{ii}(OH^{i}_{2})$	read	$Ca^{ii}(OH)^{i}_{2}$
"	17,	"	14,	"	Na_2HSO_4	"	$NaHSO_4$
"	32,	"	9,	"	$3H_2O$	"	$6H_2O$
"	44,	"	11,	"	(218)	"	(215)
"	60,	"	14,	"	$SnCl$	"	$SnCl_4$
"	64,	"	9,	"	H_2TeO_4	"	H_2TeO_3
"	71,	"	9,	"	$HC_2H_2O_2$	"	$HC_2H_3O_2$
"	71,	"	13,	"	H_2FeO_2	"	$HFeO_2$
"	79,	"	3,	"	$(NH)_4ClAq$	"	NH_4ClAq
"	115,	"	3,	"	*powder*	"	*powdered residue*
"	116,	"	10,	"	171	"	117
"	119,	"	4,	"	$(AgIO)$	"	$(AgIO_3)$
"	124,	"	25,	"	CO	"	Co
"	130,	"	2,	"	138	"	140
"	142,	"	16,	"	357	"	429

328602

PREFACE.

THE course in qualitative analysis here outlined has been followed, with slight variations, by the Freshman classes in the Colleges of Applied Science since 1893. The reduction of the number of hours allotted to this subject has made it seem advisable to spend less time at the outset on a systematic study of the reactions of the several metals and acid radicals, and a larger proportion on actual analytical work following a given scheme for separation and detection. This certainly retains the interest of students and apparently leads to the same end, if care is taken to emphasize the principles on which the methods are based. The notes in Part 1 on the general principles involved, and in Part 5 on the analytical schemes, are intended to accomplish this result.

The author's thanks are due to Professor Rising, Professor O'Neill and to Mr. J. H. Gray, for advice and suggestions.

W. J. S.

Berkeley, December, 1897.

EDWARD BOOTH

328602

CONTENTS.

PART 1. Introduction: General Principles, Operations and Reagents, Laboratory Work.

PART 2. Reactions of the Metals.

PART 3. Reactions of the Non-metals and Acid Radicals.

PART 4. Examination of Substances of Unknown Composition.

PART 5. Notes on the System of Analysis.

ACCOMPANYING TABLES.

TABLE I. Separations of the Metals from Solutions.

TABLE II. Examination of Simple Substances.

TABLE III. Details of Precipitation of Groups from Solutions.

TABLE IV. Details of Examination of Group Precipitates:
- Silver Group Pp. I.
- Calcium Group Pp. V.
- Residual Solution VI.

TABLE V. Iron Groups Pps. III, IV, and III A.

TABLE VI. Copper and Arsenic Groups Pp. II.

The reference numbers throughout book indicate paragraphs or sections, the first numeral referring to the part of book in which the paragraph is found.

PART I.

INTRODUCTION.

101 THE WORD *Analysis*, used in chemistry to signify the resolution of a compound into simpler compounds or into its elements, as opposed to synthesis, is also applied to the determination of the composition of substances. *Qualitative Analysis* determines the nature of the constituents of a body; *Quantitative Analysis* determines the proportion of some or all of these constituents. Either may be *Partial*—referring to the principal, or to certain particular constituents, or *Complete* when it is attempted to consider all the components. Again, either may be *Ultimate*—referring to the elements contained, or *Proximate*—referring to certain groups of elements.

102 Qualitative analysis may be applied:

1. To find out the essential composition of a comparatively simple substance, such as a metal or a salt.
2. To determine all the constituents of a more or less complex substance or mixture of substances.
3. To prove the presence or absence of some particular body in a given substance, as arsenic in food or silver in an ore, disregarding all other constituents of the substance.

103 To detect the presence of particular substances, to distinguish them from one another, or to separate them, we depend upon the existence of certain *properties*, every substance, elementary or compound, possessing a certain combination of properties different from that possessed by any other.

The properties most readily recognizable are:—

1. State of Aggregation: Solid, liquid, or gaseous.
2. Color.
3. Effects of Heat: Change of color, fusion, volatilization, decomposition.
4. Solubility: (*a*) In water, forming simple solutions.
    (*b*) In acids, forming soluble salts with the acid used.
    (*c*) In solutions of alkalis (alkaline hydroxides) forming salts of the alkali metals.
    (*d*) In solutions of certain salts, especially ammonium chloride and potassium cyanide, forming double salts of the alkali metals.
5. Effects of Reagents (other than solvents) tending to decompose them, these effects being indicated by the nature of the decomposition products; *e. g.*, the reduction of metals from salts or oxides, and the precipitation of insoluble substances from solutions.

Other properties less universally applicable for the purpose of recognition are:

6. Taste, Odor, Density, Action on Light (transparency, refractivity, polarization), Effects of Light (change of color, etc.), Combustibility (in air or oxygen).
7. Observed in *SOLIDS:* Crystalline Form and Habit, Lustre, Hardness, Malleability, Fracture.
8. Observed in *LIQUIDS:* Viscosity, Effect on Color of Litmus (turning it red or blue, or bleaching), Boiling Point.
9. Observed in *GASES:* Power to Support Combustion (of carbon, etc.).

Characteristic properties: Some few substances possess certain particularly conspicuous properties which at once distinguish them from nearly all others; thus the odor of hydrogen sulphide and of ammonia, the color of iodine vapor, the power of hydrofluoric acid to attack glass, are all highly characteristic of these bodies.

104 Every known substance can be identified if a sufficient number of its properties are noted; the first three or four mentioned, with the effects of a few reagents, suffice in nearly all cases.

If the presence of any particular *compound* is proven, the presence of its components follows as a matter of course.

For instance, silver chloride is a white solid which fuses without decomposition when heated, it is darkened by sunlight and is practically insoluble in water or acids but soluble in ammonia water. A substance found to possess all these properties may be safely assumed to be silver chloride. Further, if we add a solution of a known silver compound to a solution under examination, and obtain a precipitate recognized as silver chloride, we prove the presence of chlorine in the solution examined; conversely, by adding a solution of a chloride and obtaining a similar precipitate we can detect the presence of silver in another solution.

105 In some instances it is possible, by means of characteristic properties or reactions, to recognize a particular element or compound while combined or mixed with a number of others, but with complex mixtures it is, as a general rule, necessary to first separate other substances at least partially, and frequently this must be done in several stages.

106 Some skill in manipulation, as well as a knowledge of the principles of chemistry, is necessary in this work. Before commencing, the student should review his knowledge of general chemistry and of chemical nomenclature.* Although a sufficient acquaintance with the general laws of chemistry is assumed on the part of the student, some of the more important generalizations and rules of nomenclature are here given for convenient reference. It is to be noted that a rigid definition is seldom possible in chemical classification and nomenclature.

---

* See Remsen, ch. I, VI, and X.

107 An *element* is a substance which cannot by known means be resolved into simpler substances, while a *compound* is made up of two or more elements. Of the seventy-five elements so far recognized (see 112) compounds of about one-half will be studied in the present course. A *molecule* of a compound, for the present purposes, will be understood to be the smallest portion capable of taking part in the reaction involved in any chemical change, and the *atom* of any element the smallest portion entering into a molecule.

The formulas used indicate the simplest possible constitution of the molecules, each symbol representing an atom. The symbol aq following a formula indicates one molecule of combined water, Aq means that the substance represented is in water solution.

An *equation* is intended to represent a reaction which goes on between the substances indicated by symbols in its left hand member, producing those indicated in the right hand member, the same numbers of atoms appearing in each case, but differently arranged; but it must be understood that the changes represented by an equation do not always go on to completeness, and that an equation which strictly represents the changes taking place under one particular set of conditions does not necessarily represent those taking place between the same substances under other conditions, or taken in different proportions (see 124–126), also that in some cases several reactions may take place side by side between the same substances.

108 When a compound in solution is electrolyzed—as for instance by introducing platinum wires connected with the zinc and carbon plates of a battery—those elements or groups of elements which tend to travel to the cathode, the pole connected with the zinc, are called *positive radicals* or cathions; those which travel to the anode are *negative radicals* or anions.

The positive radicals thus travel with the positive current. The ions or radicals do not always appear as such in electrolysis but may give rise to other substances, either by decomposing the solvent or by combining with the substance of the anode or cathode. The most positive elements are potassium, sodium and the allied metals, followed by Ba, Sr, Ca, Mg, and the other metals and hydrogen. The most negative are the elements chlorine and oxygen, followed by the remaining non-metals. Compound radicals are such groups of elements as (NH_4), (SO_4), (CN), which travel together when their solutions are electrolyzed.

In all metathetical reactions (123), and in most of the reactions used in qualitative analysis, except some of those involving oxidation and reduction (122), the portions transferred from one molecule to another correspond to the radicals or ions separated by electrolysis.

109 *The Valence of an element* is measured by the *number of atoms* of H, or of Cl, *which one of its atoms combines with, or replaces.* It may be regarded as the *number of bonds* or "units of chemical affinity," *which its atom exercises.* (See Remsen, pages 82 and 428.) Thus in the Ferric salts (as $FeCl_3$, Fe_2O_3), iron is tri-valent or a triad element, its atom replacing three atoms of H: in the Ferrous salts ($FeCl_2$, FeO) it is divalent, or a dyad, one atom replacing two atoms of the H of HCl or H_2O. The valence of a compound radical is the number of bonds available for combining with other elements or groups: thus (NH_4) is a monad positive radical, (SO_4) is a dyad negative radical.

Valence is indicated where necessary by dashes or Roman numerals, thus: Fe^{III}, Fe^{II}, Cr^{VI}, $(PO_4)^{III}$, $(NO_3)^{I}$.

110 *Acids.* Most acids belong to one of two classes:*

1. *Hydracids*, which contain hydrogen, united with a non-metal or negative element, as HCl, H_2S, HF.
2. *Oxyacids*, containing hydrogen combined with oxygen and another of the more negative elements, as HNO_3, H_2SO_4, H_3AsO_4.

Acid radicals are the elements or groups which, with H, form acids; these correspond to the negative ions of electrolysis.

---

*See also 120.

Anhydrides are oxygen acids minus water, as N_2O_5, SO_3, As_2O_5, and are sometimes spoken of as acids.

The strongest acids are, HCl, HNO_3, H_2SO_4, HBr, HI, $HClO_3$, followed by HF, H_3PO_4, $HC_2H_3O_2$, H_2SO_3; weak acids comprise H_2CO_3, H_2S, HCN, and most others. The stronger acids are soluble in water and redden litmus, the weaker having little or no effect.

The term *base* is applied to metallic hydroxides and a few other compounds which react with acids to form salts. A base usually contains a metal or positive radical united with oxygen and hydrogen, and may be regarded as a metallic oxide combined with water: *e. g.*, KOH, $Zn(OH)_2$, $Bi(OH)_3$, BiO(OH), $(NH_4)(OH)$.

The strongest bases are the caustic alkalis, hydroxides of the more positive metals, KOH, NaOH, etc., and $(NH_4)OH$, all of which are highly soluble in water—their solutions turning red litmus blue—and the alkaline earths $Ba(OH)_2$, $Sr(OH)_2$, $Ca(OH)_2$, $Mg(OH)_2$, which are less soluble in water in the order named, but readily turn litmus blue. Most other bases are nearly insoluble in water and affect litmus only feebly or not at all.

A *salt* is formed, together with water, when an acid reacts with a base. A salt corresponds to an acid in which the H is replaced wholly or partly by metal, or to a base in which hydroxyl is replaced by an acid radical. Salts may be regarded as compounds of positive with negative radicals.

There are many cases in which metals will not *directly* displace the hydrogen of acids (thus silver and platinum are not affected by HCl), and in some instances the replacement can not be brought about at all, so that the salts of certain metals with certain acid radicals are at present unknown.

Generally, *negative radicals with hydrogen form acids; positive radicals with hydroxyl (OH) form bases; positive and negative radicals together form salts.*

Acids, bases, and salts may thus be considered as a continuous series of binary compounds of positive elements or groups with negative, regarding acids as salts of the metal H, and hydroxides as salts of the acid H(OH), water forming a connecting link between acids and bases, thus H_2SO_4 is hydrogen sulphate, and KOH potassium hydrate. See Remsen, page 146.

111 LIST OF KNOWN ELEMENTS.

The atomic weights are those calculated by F. W. Clarke, 1897, the weight of an atom of oxygen (16.00) being the standard, and the valences are those exhibited in the more important compounds.

Name.	Symbol and Valence.	Atomic Weight.	Name.	Symbol and Valence.	Atomic Weight.
Aluminium	Al^{III}	27.1	Molybdenum	$Mo^{VI\ IV}$	96.
Antimony	$Sb^{III\ V}$	120.4	Neodymium	$Nd^{III\ IV}$	140.8
Argon	A	?	Nickel	Ni^{II}	58.7
Arsenic	$As^{III\ V}$	75.	Niobium see Columbium.		
Barium	Ba^{II}	137.4	Nitrogen	$N^{V\ III}$	14.
Beryllium see Glucinum.			Osmium	$Os^{II\ to\ VIII}$	191.
Bismuth	Bi^{III}	208.1	Oxygen	O^{II}	16.00
Boron	B^{III}	11.	Palladium	Pd^{II}	106.4
Bromine	$Br^{I\ VII}$	80.	Phosphorus	$P^{V\ III}$	31.
Cadmium	Cd^{II}	112.	Platinum	Pt^{IV}	194.9
Calcium	Ca^{II}	40.	Potassium	K^{I}	39.1
Carbon	C^{IV}	12.	Praseodymium	$Prd^{III\ IV}$	143.6
Cerium	$Ce^{III\ IV}$	140.2	Rhodium	$Rh^{II\ III\ VI}$	103.
Cesium	Cs^{I}	132.9	Rubidium	Rb^{I}	85.
Chlorine	$Cl^{I\ V\ VII}$	35.45	Ruthenium	$Ru^{II\ III\ VI}$	101.7
Chromium	$Cr^{III\ VI}$	52.	Samarium	Sa^{III}	150.
Cobalt	Co^{II}	58.9	Scandium	Sc^{III}	44.
Columbium	Cb^{V} or Nb	93.7	Selenium	$Se^{II\ IV\ VI}$	79.
Copper	$Cu^{II\ I}$	63.6	Silicon	Si^{IV}	28.4
Erbium	Er^{III}	166.3	Silver	Ag^{I}	107.9
Fluorine	F^{I}	19.	Sodium	Na^{I}	23.
Gadolinium	Gd^{III}	156.8	Strontium	Sr^{II}	87.6
Gallium	Ga^{III}	69.9	Sulphur	$S^{II\ IV\ VI}$	32.
Germanium	Ge^{IV}	72.5	Tantalum	Ta^{V}	182.8
Glucinum	Gl^{II} or Be.	9.1	Tellurium	$Te^{II\ IV}$	127.5
Gold	Au^{III}	197.	Terbium	Tb^{III}	160.
Helium	He	?	Thallium	$Tl^{I\ III}$	204.1
Hydrogen	H^{I}	1.008	Thorium	Th^{IV}	232.6
Indium	In^{III}	113.9	Thulium	Tu^{III}	170.7
Iodine	$I^{I\ VII}$	126.8	Tin	$Sn^{IV\ II}$	119.
Iridium	$Ir^{III\ IV}$	193.	Titanium	$Ti^{IV\ III}$	48.1
Iron	$Fe^{III\ II}$	56.	Tungsten	W^{VI}	184.8
Lanthanum	La^{III}	138.6	Uranium	U^{VI}	239.6
Lead	Pb^{II}	207	Vanadium	V^{V}	51.4
Lithium	Li^{I}	7.	Ytterbium	Ytb^{III}	173.2
Magnesium	Mg^{II}	24.3	Yttrium	Yt^{III}	89.
Manganese	$Mn^{II\ III\ to\ VII}$	55.	Zinc	Zn^{II}	65.4
Mercury	$Hg^{II\ I}$	200.	Zirconium	Zr^{IV}	90.4

112. Table showing Usual Valence of Important Elements.

	MONADS	DYADS	TRIADS	TETRADS	PENTADS	HEXADS	HEPTADS	
NON-METALS —	HR HALOGENS: Fluorine ......F Chlorine ..... Cl Bromine .....Br Iodine...........I Cyanogen * Cy	H_2R Oxygen ....O Sulphur ... . S	R_2O_3, H_3RO_3 Boron ....B	RO_2, H_2RO_3 Sulphur............S Silicon ....Si Carbon.............C	R_2O_5, HRO_3 Nitrogen..........N Phosphorus......P Chlorine...........Cl Bromine...........Br Iodine ....I (in Chlorates, etc.)	RO_3, H_2RO_4 Sulphur.............S Manganese .....Mn Chromium.......Cr (in Sulphates, etc)	R_2O_7, HRO_4 Chlorine.........Cl Manganese .....Mn (in Perchlorates, etc.)	ACID
			RH_3, R_2O_3 Nitrogen ....N Phosphorus......P					
	R_2O, R_2S, RCl Hydrogen......H Silver ....Ag Mercury(ous) Hg (Copper(ous)..Cu)	RO, RS, RCl_2 Stannous Tin..Sn Mercury (ic)...Hg Lead .... Pb Copper (ic)......Cu Cadmium.......Cd Cobalt............Co Nickel ....Ni Ferrous Iron...Fe Manganese ...Mn Zinc ....Zn	RH_3, R_2O_3, R_2S_3, (RCl_3) Arsenic(ous)....As Antimony(ous) Sb	RO_2, RS_2, RCl_4 Platinum (ic)...Pt Stannic Tin......Sn	R_2O_5, R_2S_5, (RCl_5) Arsenic (ic)......As Antimony (ic).Sb			
			R_2O_3, R_2S_3, RCl_3 Gold (Auric)....Au Bismuth..........Bi	RO_2, (RCl_4) (Lead............Pb) (Manganese..Mn)				
+ METALS	Ammonium* NH_4 Lithium. .....Li Sodium...... Na Potassium.....K	RO, RCl_2, (RS) Magnesium....Mg Calcium.........Ca Strontium......Sr Barium ....Ba	R_2O_3, RCl_3 Aluminium ......Al Chromium (in Chromic Salts) Cr Ferric Iron......Fe (Mn & Co rarely)					BASIC

The symbols HR, RO, etc., show the leading types of compounds formed by the elements under them.

* The group (CN) or Cy acts as an acid radical; (NH_4) or Am as a metal or basic radical; the group (OH)—*hydroxyl*-acts as a monad radical, combining with all oxide-forming elements.

113 PERIODIC ARRANGEMENT OF THE ELEMENTS

In the Order of their Atomic Weights.

GROUPED ACCORDING TO VALENCE (AFTER LOTHAR MEYER).

Group	I	II	III	IV	V	VI	VII	VIII
Series								
1	H							
2	Li	Be	B	C	N	O	F	
3	Na	Mg	Al	Si	P	S	Cl	
4	K	Ca	Sc	Ti	V	Cr	Mn	Fe, Co, Ni, Cu
5	Cu	Zn	Ga	Ge	As	Se	Br	
6	Rb	Sr	Yt	Zr	Cb	Mo		Ru, Rh, Pd, Ag
7	Ag	Cd	In	Sn	Sb	Te	I	
8	Cs	Ba	La	Ce	Ndi	Prdi		
9								
10			Er	Yb	Ta	W		Os, Ir, Pt, Au
11	Au	Hg	Tl	Pb	Bi			
12				Th		U		

This table of the Natural System is inserted for comparison with that on the opposite page, and with the analytical grouping of the metals in an accompanying table (I); it will be seen that the analytical groups do not coincide with either series, but that there are marked similarities in the groupings.

114 THE MORE IMPORTANT ACIDS

Classified according to Basicity.

Monobasic	
Hydrochloric	HCl
Hydrobromic	HBr
Hydriodic	HI
Hydrofluoric	HF
Hydrocyanic	HCN
Thiocyanic	$HCNS$
Nitric	HNO_3
Nitrous	HNO_2
Chloric	$HClO_3$
Hypochlorous	$HClO$
Acetic	$HC_2H_3O_2$
Dibasic	
Hydrosulphuric	H_2S
Sulphuric	H_2SO_4*
Sulphurous	H_2SO_3
Thiosulphuric	$H_2S_2O_3$
Carbonic	H_2CO_3
Chromic	H_2CrO_4
Dichromic	$H_2Cr_2O_7$
Chloroplatinic	H_2PtCl_6
Fluosilicic	H_2SiF_6
Oxalic	$H_2C_2O_4$
Tartaric	$H_2C_4H_4O_6$
Tribasic	
Phosphoric (ortho)	H_3PO_4*
Arsenic	H_3AsO_4*
Arsenious	H_3AsO_3*
Boric	H_3BO_3*
Hydroferricyanic	$H_3Fe'''Cy_6$
Citric	$H_3C_6H_5O_7$
Tetrabasic	
Silicic (ortho)	H_4SiO_4*
Hydroferrocyanic	$H_4Fe''Cy_6$

Oxides may be regarded as derived from dibasic $H_2(O)$,* hydroxides from monobasic $H(OH)$.

---

*Other modifications of these exist (meta-, pyro-, etc.), formed by combination of two or more molecules of the ortho-acids and removal of water.

115 *The basicity of an acid* is expressed by the number of atoms of replaceable hydrogen in one molecule: thus HNO_3 and HCl are monobasic, H_2SO_4 dibasic, H_3PO_4 tribasic, H_4SiO_4 tetrabasic, etc.

The acidity of bases corresponds to the basicity of acids, and is measured by the number of hydroxyl groups in the molecule: this corresponds to the valence of the metal or basic radical contained: thus KOH is a monacid base, $Zn(OH)_2$ diacid, $Bi(OH)_3$ triacid; $(BiO)(OH)$ and NH_4OH are monacid and are the hydroxides of the compound radicals bismuthyl (BiO), and ammonium (NH_4).

In salts, including acids and bases, the numbers of bonds of the positive and negative members of any one are equal, if reckoned by multiplying the numbers of the radicals by their valences. Thus we have—

Acids: $H^{I}Cl^{I}$, $H^{I}(NO_3)^{I}$, $H^{I}_{2}(SO_4)^{II}$, $H_4{}^{I}(SiO_4)^{IV}$, $H^{I}_{2}(SiF_6)^{II}$.
Bases: $K^{I}(OH)^{I}$, $(NH_4)^{I}(OH)^{I}$, $Ca^{II}(OH)^{I}_{2}$, $Bi^{III}(OH)^{I}_{3}$, $(BiO)^{I}(OH)^{I}$, $Pb^{II}(OH)^{I}_{2}$, $Al^{III}(OH)^{I}_{3}$.
Salts: $K Cl^{I}$, $Bi^{III}(NO_3)^{I}_{3}$, $(BiO)^{I}(NO_3)^{I}$, $Al^{III}_{2}(SO_4)^{II}_{3}$, $Al^{III}(PO_4)^{III}$, $Ca^{II}_{3}(PO_4)^{III}_{2}$, $K_2(SO_4)^{II}$, $K^{I}H^{I}(SO_4)^{II}$, $Pb^{III}Cl^{I}(OH)^{I}$, $K^{I}_{2}(SiF_6)^{II}$.

The symbols of the more positive radicals being written first.

116 Salts are classified as normal, acid and basic.

In normal salts all the replaceable hydrogen of the acid is replaced by metal or positive radical, one atom of H being removed for each acting bond of the radical introduced. Hence if we know the formula or the basicity of an acid and the valence of a metal, or the acidity of a base,* we can at once write the formula of the corresponding normal salt: the number of bonds acting being the least common multiple of the numbers expressing basicity and valence. Thus Ca^{II} and H_3PO_4 form the normal salt $Ca_3^{II}(PO_4)_2^{III}$, $Al^{III}(OH)_3$ and H_2SO_4 form $Al_2^{III}(SO_4)_3^{II}$, etc.

---

*These may be found for the more important metals and acids in 112 and 114.

In *acid salts* only part of the hydrogen of the acid is replaced by metal: as in $KH(SO_4)$, $CaH(PO_4)$, $NaH(CO_3)$, etc.

When an acid forms several salts with one metal, by replacement of successive proportions of H, these are called *primary*, *secondary*, *tertiary*, etc., as a less or greater proportion of H is replaced; when only two are formed the words "acid" and "normal" suffice to distinguish them. See Remsen, page 140. Thus there are three calcium phosphates known: primary $CaH_4(PO_4)_2$, secondary $CaH(PO_4)$, tertiary or normal $Ca_3(PO_4)_2$; the sodium sulphates are: primary or acid NaHSO4 ~~Na_2HSO_4~~, secondary or normal Na_2SO_4.

Basic salts may be regarded as bases in which only part of the hydroxyl has been replaced by an acid radical, or as acids in which all the hydrogen has been replaced by metal and with which a further amount of hydroxide or oxide (base) has combined. The formulas may be written in accordance with either view: thus basic lead carbonate is $Pb_3(OH)_2(CO_3)_2$ or $2PbCO_3.Pb(OH)_2$; the latter method is usually to be preferred, as many of the precipitated "basic salts" are probably mixtures or indefinite compounds of normal salt with base.

Double salts contain a single acid radical combined with two metals, or one metal with two acid radicals, in proportions corresponding to the union of simple numbers of molecules of two single salts, *e. g.*, $KAl(SO_4)_2.12aq$, $K_2Zn(SO_4)_2.6aq$, $Pb_2CO_3Cl_2$.

117 *Reaction with indicators.*—Substances whose solutions redden litmus are said to have an *acid reaction*, but are not necessarily acids; similarly, those which turn it blue have an *alkaline reaction*, but are not necessarily bases: substances which do not affect its color are said to be neutral to litmus, or of neutral reaction.

The terms acid and basic applied to salts do not refer to their reaction with litmus, which depends on the relative "strength," as well as the proportion, of acid and base: thus Na_2HPO_4 (an *acid salt* of a strong base, with a comparatively weak acid) turns litmus blue, or has an *alkaline reaction*, while $CuSO_4$ (a *normal salt* of a weak base, with a strong acid) reddens litmus, or has an *acid reaction.* The normal salts of the more positive metals, with strong acids, are *neutral* to litmus.

Beside litmus there are many other indicators (chiefly organic substances of complex constitution, such as cochineal, methyl orange, phenol-phthalein, turmeric, etc.) which may be used to distinguish acid from alkaline substances, or to detect free acid or alkali, usually by some striking change of color.

118 *Nomenclature.*—The names of hydracids commence with *hydro-*, those of the corresponding salts, and binary compounds generally, end in *-ide;* the names of oxyacids end in *-ic* or *-ous*, and those of the corresponding salts in *-ate* and *-ite*, The terminations *-ic* and *-ous*, and the prefixes *per-* and *sub-*, *proto-*, or *hypo-*, indicate greater or less proportions of oxygen or other negative body.

ACIDS.	FORMULAS.	SALTS.
Hydrochloric	HCl	Chlorides
Hypochlorous	$HClO$	Hypochlorites
Chlorous	$HClO_2$	Chlorites
Chloric	$HClO_3$	Chlorates
Perchloric	$HClO_4$	Perchlorates
Hydrosulphuric	H_2S	Sulphides
Hydrocyanic	HCN	Cyanides
Cyanic	$HCNO$	Cyanates
Sulphurous	H_2SO_3	Sulphites
Sulphuric	H_2SO_4	Sulphates

Again, $FeCl_3$ is ferric chloride or perchloride of iron, $FeCl_2$ is ferrous chloride or protochloride of iron: the latter containing a less proportion of chlorine.

The prefix *sesqui-* is occasionally used to denote oxides containing one and a half atoms of oxygen to one of metal:

thus ferric oxide Fe_2O_3 is sometimes called sesquioxide of iron.

In naming salts it is preferable to simply prefix the name of the metal to the generic name, except when the metal forms two or more classes of salts. Thus we say sodium sulphate rather than sodic sulphate or sulphate of soda, but ferric chloride and ferrous chloride to distinguish the two chlorides of iron from one another. The metals Fe, Cr, Cu, Hg, Sn, Sb, As, Mn, form two or more classes of salts.

119 *Dualistic system of notation.*—The oxyacids, their salts, and the hydroxides may be considered, and their formulas written, as compounds of positive with negative oxides; thus (compare 115):

Acids: $H_2O.N_2O_5$, $H_2O.SO_3$, $2H_2O.SiO_2$, $3H_2O.P_2O_5$;
Bases: $K_2O.H_2O$, $CaO.H_2O$, $Bi_2O_3.3H_2O$, $Bi_2O_3.H_2O$, $Al_2O_3.3H_2O$;
Salts: normal: $3CaO.P_2O_5$, $Al_2O_3.3SO_3$, $K_2O.N_2O_5$;
acid: $2CaO.H_2O.P_2O_5$, $CaO.2H_2O.P_2O_5$, $H_2O.K_2O.2SO_3$;
basic: $3PbO.2CO_2.H_2O$, $Bi_2O_3.N_2O_5$.

This system is convenient for showing the changes of valence in oxidation, and exhibiting the composition of some complex salts (as silicates when it is difficult to trace the acid from which they are derived.

120 The prefix *thio-* (or *sulpho-*) indicates an acid or salt containing sulphur in place of the O of oxyacids: *chloro-*, *fluo-*, etc., denote a replacement of O by Cl or F, etc.

Thus KCNS is potassium thiocyanate, or sulphocyanate; K_2SiF_6 is potassium fluosilicate, derived from fluosilicic acid, H_2SiF_6, corresponding to silicic acid H_2SiO_3; Na_2CS_3 is sodium thiocarbonate, corresponding to Na_2CO_3.

In some cases several acids are derived from the same anhydride: thus ordinary sulphuric acid and the sulphates correspond to $H_2O.SO_3$: while disulphuric (pyrosulphuric) acid, $H_2S_2O_7$, and the disulphates correspond to $H_2O.2SO_3$, similarly potassium chromate (K_2CrO_4) and dichromate ($K_2Cr_2O_7$) correspond respectively to the acids $H_2O.CrO_3$ and $H_2O.2CrO_3$. There are three acids derived from the anhydride P_2O_5: orthophosphoric H_3PO_4 ($3H_2O.P_2O_5 \div 2$), pyrophosphoric $H_4P_2O_7$ ($2H_2O.P_2O_5$), and metaphosphoric HPO_3 ($H_2O.P_2O_5 \div 2$). Salts of still more complex constitution, as the thioarsenites and native silicates, are best expressed by the dualistic notation.

121 The hydroxides and oxides of the more positive metals always act as bases. Compounds of the most negative elements with oxygen or hydrogen, or with both, always act as acids. But hydroxides or oxides of some of the intermediate elements (some of the less positive metals) may act in either sense, combining with either stronger acids or stronger bases to form salts. Thus ZnO reacts with H_2SO_4 to form $ZnSO_4$ (zinc sulphate) and with KOH to form K_2ZnO_2 (potassium zincate): so that zinc hydroxide ($Zn(OH)_2$) plays the part of an acid (H_2ZnO_2) as well as that of a base.

When an element combines with oxygen in more than one proportion the higher oxide is always the more acid (or less basic) in character. Thus $Mn^{II}O$ (or $Mn(OH)_2$) is the base of the manganous salts ($MnCl_2$ etc.): $Mn^{IV}O_2$ forms scarcely any salts ($MnCl_4$, the best known, is very unstable): and $Mn^{VI}O_3$ forms no salts with acid radicals, but is itself the anhydride of manganic acid (H_2MnO_4), forming the manganates. Similarly $Fe(OH)_2$ is a comparatively strong base, $Fe(OH)_3$ a much weaker base, sometimes acting as a weak acid, as, *e. g.*, in Fe_3O_4 or $Fe^{II}O.Fe_2^{III}O_3$, ferrous ferrite.

122 *Oxidation* takes place when oxygen, or any other negative radical, combines with an element or compound; and when hydrogen, or any positive radical, is removed. It consists in an *increase of the proportion of the more negative constituents* of a substance, *i. e.*, in an increase of the acting valence of the more positive members towards oxygen or any negative radical.

Reduction is in every respect the reverse of oxidation; taking place when oxygen or any negative radical is removed from a compound, and when hydrogen or a positive radical is added.

Oxidation and reduction usually accompany each other.

123 *Metathetical reactions* are those which take place when one positive radical is exchanged for another, or one negative radical for another, or both together, the numbers of bonds of the radicals exchanged for each other being invariably equal.

Thus the equations:

$$H_2SO_4 + NaOH = NaHSO_4 + H_2O$$
$$Pb(NO_3)_2 + H_2SO_4 = PbSO_4 + 2HNO_3$$
$$Al_2(SO_4)_3 + 6KOH = 3K_2SO_4 + 2\ Al(OH)_3$$

all represent metathetical reactions, in which no oxidation nor reduction occurs.

The equation $Zn + H_2SO_4 = ZnSO_4 + 2H$ represents a case of metathesis in which one element (Zn) is oxidized, and another (H) reduced, the acting valence of the zinc increasing from 0 to 2, that of the H being reduced from 1 to 0.

The reaction $Cl + FeCl_2 = FeCl_3$ is not a case of metathesis, the iron being oxidized from the dyad to the triad condition.

124 The reactions utilized in qualitative analysis most commonly consist in the exchange of radicals for one another, giving some products easily separated from others or recognizable by certain properties.

A *reagent* is a body which, by reacting chemically with a substance under examination, indicates its composition or assists in separating some of its constituents. The so-called "chemical tests," effects of reagents, depend frequently on the formation of precipitates of characteristic colors from solutions, or on the dissolving of precipitates or other solids.

Most of the reactions to be dealt with (except in blowpipe tests, 143 *et seq.*) are between substances which are in solution, or one of which is in solution. As reactions only take place between substances in contact the liquid state is most generally favorable, and the first treatment of solids is usually to dissolve them, after dividing them so as to present as large a surface as possible.

125 Reactions between a number of substances seldom go on to completion when all the products remain in contact. For instance, the reaction between two substances in a water solution is usually incomplete, a point of equilibrium being reached at which action ceases, except in those cases in which one of the products is removed from the field of action. This removal of one of the products may take place (1) when it is *insoluble* in water and therefore *precipitated*, (2) when it is *volatile* under the existing conditions and is *vaporized*.

No very definite rules can be given to decide whether a particular reaction will or will not occur under given conditions, but the following will serve as a guide to the probability of its taking place.*

When two or more substances are brought in contact, the general tendency is for that reaction, if any, to go on, which develops the greatest possible amount of heat.

Heat may be *given out* in a reaction:
- (a) By change of state of aggregation, in the direction gas—liquid—solid (*e. g.*, by precipitation).
- (b) By the combination of two radicals, the heat of combination being greatest for those differing most widely in positive or negative character (108).
- (c) By a decrease of the total volume.

Heat may be *absorbed* by changes of a reverse character:
- (a) By change of state in the direction solid—liquid—gas.
- (b) By the splitting up of molecules of compounds or elements.
- (c) By changes involving increase of volume.

Commonly several of these changes take place together, the total heat effect being the *algebraic sum* of the heat effects of each change taken singly. In *exothermic* reactions heat is, on the whole, given out: in *endothermic* reactions heat is absorbed.

The tendency is therefore, dealing with solutions, for the most positive radicals to combine with the most negative (*i. e.*, an alkali-metal in solution tends to combine with the strongest acid radical present) *and also for precipitates to form. The*

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*Compare Remsen, chap. XXIII.

more stable compounds, such as water, tend to be produced whenever possible.

The following are cases of special importance in analytical work.

Salts of the alkali-metals are soluble in water, almost without exception, but most salts of the heavy metals with weak acids (carbonates, hydroxides, sulphides) are insoluble: hence *on mixing a solution of an alkaline hydroxide, sulphide, or carbonate, with a solution of the chloride, nitrate, sulphate, or acetate of a heavy metal, a reaction occurs and a precipitate is almost invariably formed.*

When a free acid is present with other salts in a solution, and a free alkaline hydroxide is added, or vice versa, *the first effect invariably includes the neutralization of the acid and alkali by each other.*

At high temperatures non-volatile acids tend to displace more volatile ones, even though stronger: the same is true of bases.

126 The *action of mass* must be kept in view in analysis, the addition of a considerable excess * of one reacting substance tends to carry the change in the other to completion: in general, a slight excess of reagent is necessary to bring about a given change, while a large excess may cause further reactions to take place.

The effect of varying conditions must also be noted, especially of *temperature* and *concentration.* The *presence of free acid or alkali* frequently exerts an important effect. In some cases also the presence of a very small proportion of free acid, or of some salt as NH_4Cl, influences reactions or makes it possible for them to take place, while itself undergoing no apparent change.

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* By *excess* an indefinitely large amount is not meant, but somewhat more than the minimum. Addition of a very large excess of reagents is nearly always injurious.

Chemical changes do not go on instantaneously, many requiring a considerable time before equilibrium is reached. Application of heat—raising the temperature moderately—accelerates reactions. Those reactions in which much heat is evolved therefore tend to go on very rapidly: while endothermic reactions usually require heat to be supplied, in order to induce them to go on to any appreciable extent. On the other hand, most compounds are decomposed if exposed to an extremely high temperature.

The following experiments may be made to illustrate mass action, and the effect of varying conditions upon equilibrium:

Add a little H_2SAq to a solution of $SbCl_3$ in HClAq: then heat the mixture strongly. In a cool solution the equation

$$2SbCl_3Aq + 3H_2SAq = Sb_2S_3 + 6HClAq$$

represents the changes taking place; when heated the reaction is reversed.

Take one or two ccs of dilute KCNSAq, add a few drops of $FeCl_3Aq$, then $HgCl_2Aq$ until the color almost disappears, then add more $FeCl_3Aq$. Since $Fe(CNS)_3$ is colored and $Hg(CNS)_2$ colorless, both being soluble in water, it is easy to see with which metal the (CNS) radical is chiefly combined when either metal is in excess of the other.

To a solution of As_2O_3 in water add H_2SAq in considerable excess, allow to stand some minutes, examine, then add a few drops of HClAq and warm gently.

Take three tubes containing a water solution of As_2O_3, to one add a little HClAq, make a second alkaline, then to each add equal quantities of H_2SAq, warm gently and examine after standing a few minutes.

Treat three tubes of $NiSO_4Aq$ in the same way, using ammonia to make the solution just neutral in the third case and strongly alkaline in the second.

OPERATIONS.

127 The most important operations in analysis are: the *solution* of solids in liquids, the *precipitation* of solids from solutions, the separation of a precipitate or other solid from a liquid by *filtration* or by *decantation*, the *washing* of a precipitate or solid residue to remove the adhering liquid and the dissolved matter contained in it, the *evaporation* of a liquid to reduce its bulk, concentrate its contents, or obtain the contained solids in the form of a residue, the *distillation* of volatile liquids, and the *ignition*, *sublimation*, and *fusion* of solids.

128 To dissolve a solid, the finely divided substance is digested with the solvent with the aid of heat, usually in a test-tube or small flask or beaker: solution may be complete or partial; any residue may be treated with other solvents or with fresh portions of the same.* Acids used for solution should not be too highly concentrated, as many salts are less soluble in water in presence of the corresponding acids; *e. g.*, NaCl is nearly insoluble in concentrated HClAq.

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*Simple solution is said to occur with solvents such as water or alcohol when the evaporation of the liquid leaves the substance unchanged in composition: solution with decomposition may occur with "chemical solvents" which by reacting yield new compounds soluble in water: thus $CaCO_3$ dissolves in HClAq to form a water solution of $CaCl_2$. The solubility of a substance is not to be confused with the rate of solution: the former refers to the maximum mass capable of being dissolved by a given quantity of solvents, the latter to the mass dissolved in a given time: the solubility of solids usually increases, that of gases decreases, with rising temperature: the *rate* of solution varies with the surface exposed to solvent, and is increased by stirring or agitation and also by heating in the case of solids; heat bringing currents of fresh solvent to bear on the surface, and also supplying the "latent heat of liquefaction," as well as increasing the solubility in the case of simple solutions and facilitating the reactions in the case of "chemical solutions."

129 *Precipitation* is effected by the addition of a reagent which yields a product insoluble* in the liquid present, secondary products usually remaining in solution: generally one salt reacts with another metathetically, or one element displaces another from a salt. Test-tubes or small beakers are the most convenient vessels.

Precipitation is much more rapid if the reacting solutions are heated; heating and shaking also facilitate the settling and separation of precipitates (by making them more dense and removing entangled bubbles of air, H_2S, CO_2, etc., which often cause them to float), making the subsequent filtration more rapid. Digestion for some time at a gentle heat increases the size of the particles and favors filtration. Precipitates are classed as *pulverulent*, *crystalline*, *flocculent*, *curdy*, *gelatinous* etc., but the character often varies considerably with the temperature and concentration of solutions. An *opalescence*, *cloud* or *turbidity* is due to the formation of a slight precipitate in a disproportionately large amount of liquid.

130 *Filtration* is carried out by passing the liquid through porous paper, or a loose asbestos plug supported in a funnel to retain the solid matter: the paper is first wetted to decrease the size of the pores by causing the fibre to swell; wetting also lessens the tendency of the paper to retain soluble matter The liquid is guided by a glass rod to the middle of the filter.

To hasten filtration, liquids should always be heated, unless there is some reason to the contrary (*e. g.*, in removing $PbCl_2$); as heating greatly reduces the viscosity: the clearer portion should be poured on first and allowed to run through before adding the portion containing precipitate; if this is not done, much time is lost, as a layer of solid matter accumulates on the paper, and the liquid has to filter through both. Fine and gelatinous precipitates particularly tend to clog the filter and retard the operation; this is to some extent remedied by previous heating. With finely divided precipitates, the *filtrate* may be turbid at first; it is then passed a second or third time over the *same* filter, the size of the pores being gradually reduced by the accumulated particles.

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*It is to be noted that no precipitates are absolutely insoluble in water, though some (*e. g.*, $BaSO_4$ or AgCl) require several thousand times their weights of water to effect solution, a proportion which may be modified by the presence of acids or other compounds.

Precipitates are *washed* by successive portions of water, allowing each to run off before adding the next: if precipitate is large, the wash water is added before putting the bulk of it on the filter and is decanted upon the filter; hot water is more effective than cold, as well as passing through more rapidly.

Some precipitates tend to pass through the filter when washed, owing to solubility in pure water; this is partly remedied by the addition of some inert salt, or any acid which does not react on the precipitate, most precipitates being less soluble in presence of other dissolved salts.

131 *Evaporation* is best carried on at a gentle heat, not allowing the liquid to boil, and in a shallow vessel, so as to expose the largest possible surface and to remove the resulting vapor as rapidly as possible. Evaporation to dryness must not be carried on in beakers, except over a water bath, but they may be used if the depth of liquid is considerable: porcelain dishes may be safely heated directly over a Bunsen burner or coal-oil lamp, or on a sand-bath: a watch-glass heated on a water-bath is convenient for very small quantities of liquid.

132 *Ignition* and *fusion* are performed by strongly heating in small porcelain or platinum dishes, or with small quantities in glass tubes. Sublimation is usually carried out on a small scale in glass tubes. See 148.

Solids are also heated occasionally in currents of gases as H, Cl, or H_2S, passed over them in glass tubes or in crucibles, and the residues or condensed volatile products examined.*

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* For details of operations see Fresenius, sections I and II.

133 All vessels used should be scrupulously clean; they are best cleansed immediately after using, rinsed once or twice with distilled water, and left to drain and dry rather than wiped. Precipitates adhering to vessels can usually be removed by rubbing with a piece of soft rubber tube, about ¾ inch long, fixed at the end of a glass rod.

REAGENTS.

134 Reagents may be classified roughly as solvents, precipitants, and oxidizing, or reducing agents.

Solvents take up solids to form homogeneous liquids.

- *Solvents forming simple solutions*, especially water.
- *Acids*, forming soluble corresponding salts.
- *Solutions of alkaline hydroxides*, forming salts of the alkali metals.
- *Solutions of alkaline sulphides*, forming thio-salts of alkali metals.
- *Solutions of alkali metal salts* (as NH_4Cl or KCN) forming double salts.

Precipitants throw down insoluble substances from solutions.

(*a*) *For metallic radicals; solutions of salts whose acid radicals form insoluble compounds with them:* compounds of H, (NH_4), Na, or K are to be preferred, especially the first two, as they may be removed by evaporation and ignition and introduce no metals which can interfere with subsequent tests of the solution. *Reducing agents* often precipitate the metals in the free state.

(*b*) *For acid radicals; solutions of salts whose metallic radicals form insoluble compounds with them:* those of Ba, Ag, and Pb are most used, and occasionally those of Fe, Cu, Hg and Ca.

Oxidizing agents tend to add oxygen or a negative radical, or to set negative elements free. Those most used are Br, Cl, HNO_3, HNO_2, aqua regia, $KClO_3 + HClAq$ and, in the dry way, $KClO_3$ and peroxides or nitrates.

Reducing agents tend to remove oxygen or a negative radical, and to set metals free.

- *The more positive metals*, as Zn, Al, or Fe (which may act directly or by evolving nascent H), and occasionally Cu or Hg.
- *Salts of metals capable of a higher degree of oxidation*, as $SnCl_2$ and $FeSO_4$.
- SO_2 and H_2S are occasionally used and, *in the dry way*, C, KCN, or Mg.

135 LIST OF PRINCIPAL REAGENTS.

Reagents Used in the Liquid State or in Water Solution.

Hydrochloric acid, H chloride
HCl (concentrated and dilute†)
Nitric acid, H nitrate...... ......
HNO_3(concentrated and dilute†)
Sulphuric acid, H sulphate.....
H_2SO_4(concentrated and dilute†)
Acetic acid, H acetate...$HC_2H_3O_2$
Hydrogen sulphide water.. .....
....................H_2S (saturated)
Aqua Regia, Nitro-hydrochloric acid*...($3HCl+HNO_3=NOCl+Cl_2+2H_2O$)
Ammonium hydroxide.....NH_4OH
chloride..........NH_4Cl
carbonate...$(NH_4)_2CO_3$
hydrogen carbonate.........NH_4HCO_3
sulphide........$(NH_4)_2S$
polysulphide (yellow)... $(NH_4)_2S_x$
oxalate.....$(NH_4)_2C_2O_4$
sulphate ....$(NH_4)_2SO_4$
acetate.....$NH_4C_2H_3O_2$
molybdate..........$(NH_4)_2MoO_4+HNO_3$
Potassium hydroxide.......... KOH
cyanide......KCN, KCy
ferrocyanide...$K_4Fe^{II}Cy_6$
ferricyanide...$K_3Fe^{III}Cy_6$
thiocyanate... .. ..$KCNS$
iodide....................KI
permanganate...$KMnO_4$
nitrite................KNO_2

Sodium hydroxide..............$NaOH$
carbonate.............Na_2CO_3
hydrogen phosphate... ....Na_2HPO_4
hypochlorite. ....$NaClO$
Barium hydroxide...........$Ba(OH)_2$
nitrate...............$Ba(NO_3)_2$
chloride.................$BaCl_2$
Calcium chloride..................$CaCl_2$
sulphate..$CaSO_4$ (saturated)
Silver (Argentic) nitrate.....$AgNO_3$
Lead (Plumbic) acetate........... .... $Pb(C_2H_3O_2)_2$
Mercuric chloride...............$HgCl_2$
Cupric sulphate.................$CuSO_4$
Stannous chloride................$SnCl_2$
Ferric chloride...................$FeCl_3$
Ferrous sulphate................$FeSO_4$
Cobalt nitrate..................$Co(NO_3)_2$
Magnesia mixture, ammonium magnesium chloride......... ......$MgCl_2+2NH_4Cl+NH_4OH$
Chloroplatinic acid...........H_2PtCl_6
Fluosilicic acid ....H_2SiF_6
Sulphurous acid..SO_2Aq (saturated)
Oxalic acid*.................... $H_2C_2O_4$
Tartaric acid*...............$H_2C_4H_4O_6$
Bromine water......................$BrAq$
Chlorine water.....................$ClAq$
Alcohol...............C_2H_5OH (95°/₀)
Starch paste*...................$C_6H_{10}O_5$
Carbon disulphide..................CS_2

The water used in analysis must be distilled.

Reagents Used Dry or in the Solid State.

Sodium carbonate (soda)...Na_2CO_3
Sodium potassium carbonate (fusion mixture)........$NaKCO_3$
Sodium borate (borax) $Na_2B_4O_7 10aq$
Sodium ammonium hydrogen phosphate (microcosmic salt, phosphor salt) $NaNH_4HPO_4.4aq$

Potassium chlorate.............$KClO_3$
nitrate................KNO_3
cyanide .... KCN
{ acid sulphate. $HKSO_4$
{ or disulphate...$K_2S_2O_7$
Barium carbonate................. $BaCO_3$ (suspended in water)

Carbon and metallic Mg, Zn, Al, Fe and Cu are occasionally used for reducing, and Ag for detecting S.

H_2S, SO_2 and CO_2 are occasionally used in the gaseous state.

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*These reagents are best mixed immediately before use.

†Dilute acids are to be used unless the concentrated are specified.

For preparation of reagents see Fresenius, Section II.

136 *General reagents or group reagents* are those which separate a considerable number of radicals (a group) at one operation, usually by precipitating them; *special reagents* are used to test for particular substances or to further subdivide groups.

The effects of the more important general reagents upon *solutions* of salts of the commoner metals are given in the following paragraphs—moderately dilute and approximately neutral solutions being understood.*

Traces of impurities occur in most reagents, however carefully prepared; most of these may be neglected except in the most refined analyses, but the following radicals are frequently present in appreciable quantities; when found in analysis the reagents used should be carefully tested for them.

In hydrochloric acid Fe, As; in nitric acid —Cl; in sulphuric acid Pb, As, Fe, $—NO_3$; in potassium or sodium hydroxides Al, $—CO_3$, $—SO_4$, —Cl; in ammonia $—CO_3$; in ammonium chloride Fe; in sodium carbonate $—SO_4$, —Cl; in barium nitrate —Cl; in metallic zinc As and Fe.

137 *Sodium carbonate* precipitates all the metals (arsenic and the alkali metals excepted) as carbonates or as basic salts; some of these change into oxides or hydroxides with escape of CO_2.

All these precipitates are decomposed or dissolved by dilute acids, with formation of water, or water and CO_2.

$$CaCl_2Aq + Na_2CO_3Aq = CaCO_3 + 2NaClAq$$
$$2SbCl3Aq + 3Na_2CO_3Aq = Sb_2O_3 + 3CO_2 + 6NaClAq$$
$$SnCl_2Aq + Na_2CO_3Aq = Sn(OH)_2 + CO_2 + 2NaClAq + H_2O$$

Nearly every salt, soluble or insoluble, when boiled with a solution of Na_2CO_3 gives up its acid radical to the sodium, which retains it in solution, the base remaining as insoluble carbonate or oxide.

Salts insoluble in acids mostly give up their acid radicals when fused with dry Na_2CO_3, and on extracting with water the acid radicals pass into solution as sodium salts K_2CO_3 and $NaKCO_3$ answer the same purpose.

In many cases, but not in all, the corresponding salts of K, Na, and NH_4 may be used interchangeably.

**In presence of free acid* the first effect of any of the five first mentioned reagents—Na_2CO_3, KOH or NaOH, NH_4OH, $(NH_4)_2CO_3$ and usually of $(NH_4)_2S$—is to neutralize the free acid.

138 *Caustic alkalis* (either sodium or potassium hydroxide may be used) precipitate as hydroxides or oxides all the metals except the alkalis, As, Ba, Sr and Ca. The three latter are precipitated from strong solutions. An insufficiency often throws down a basic salt at first, converted into an oxide or hydroxide by an excess or by heating, the hydroxides of the less positive metals showing a tendency to give up water and pass into oxides.

$$Al_2(SO_4)_3Aq + 6KOHAq = 3K_2SO_4Aq + 2Al(OH)_3$$

$$2AgNO_3Aq + 2KOHAq = 2KNO_3Aq + Ag_2O + H_2O$$

All these precipitates are converted into salts by dilute acids. Those of Sn, Pb, Sb, Al, Cr, and Zn dissolve in an excess of KOHAq, forming potassium stannate or stannite, plumbite, chromite, zincate, etc.

$$Al(OH)_3 + KOHAq = KAlO_2Aq + 2H_2O$$

These precipitates again form on carefully *neutralizing* the alkaline solutions, or on adding NH_4ClAq.

$$KAlO_2Aq + HClAq + H_2O = KClAq + Al(OH)_3$$

$$KAlO_2Aq + NH_4ClAq + H_2O = KClAq + NH_3Aq + Al(OH)_3$$

The precipitates of Ag, Cu, Cd, Zn, Ni, and Co are more or less soluble in NH_4OHAq, those of Cu, Cd, Zn, Ni, Co, Mn and Mg dissolve in NH_4ClAq, and any of these eight in a mixture of both.

139 *Ammonium hydroxide* precipitates more or less completely all the metals except the alkalis, Ba, Sr, Ca, and As.

Most of these are precipitated by reactions similar to those of KOH as basic salts, hydroxides, or oxides; but a few (*e. g.*, Hg) as amides or complex ammonium salts:

$$HgCl_2Aq + 2NH_4OHAq = NH_2Hg''Cl + NH_4ClAq + 2H_2O$$

The precipitates of Ag, Cu, Cd, Ni, Co, Zn redissolve readily when an excess of ammonia is added, those of Cr and Al very slightly: those of Mn and Mg, and of Zn, Ni, and Co, (and Fe'' to some extent) dissolve in NH_4ClAq which acts by forming double chlorides, *e. g.* $(NH_4)_2MnCl_4$, and in solutions of other ammonium salts, which prevent their precipitation if previously added, but facilitate precipitation of Fe''', Al, and Cr.

The precipitates are generally decomposed or dissolved by dilute acids.

Ammonium carbonate precipitates the same metals as NH_4OH as carbonates or basic carbonates, the reactions generally corresponding to those of Na_2CO_3, and the solubilities of the precipitates being similar to those formed by NH_4OH. Ba, Sr, and Ca are also precipitated as carbonates, slightly soluble in NH_4ClAq but dissolved by dilute acids.

140 Normal *ammonium sulphide* [$(NH_4)_2S$] is prepared by saturating the hydroxide with H_2S (forming NH_4HS) and then adding more NH_4OHAq: when exposed to light it becomes yellow and contains polysulphide [$(NH_4)_2S_x$]: the latter may be also made by digesting the normal sulphide with a little free sulphur. From neutral or slightly acid solutions $(NH_4)_2S$ precipitates all the heavy metals as *sulphides*, and Cr and Al as *hydroxides* with escape of H_2S.

$$MCl_2Aq + (NH_4)_2SAq = MS + 2NH_4ClAq$$

$$Al_2(SO_4)_3Aq + 3(NH_4)_2SAq + \cancel{4}6H_2O = 2Al(OH)_3 + 3(NH_4)_2SO_4Aq + 3H_2S$$

The precipitates of As, Sb, and Sn dissolve readily in an excess of yellow ammonium sulphide, those of Ni and Cu are slightly soluble; the solutions contain thio-salts (sulpho-salts)—ammonium thiostannate, thio-arsenite, etc. On acidulating these solutions the sulphides are again precipitated.

Hot nitric acid attacks all the precipitated sulphides except HgS, usually forming nitrates, free S and oxides of N (chiefly NO), some of the S being also oxidized to SO_3; the equations

$$3M''S + 8HNO_3 = 3M(NO_3)_2 + 3S + 2NO + 4H_2O \text{ and}$$

$$S + 2HNO_3 = H_2SO_4 + 2NO$$

partially representing the changes: more or less NO_2 is often formed when the acid is concentrated. The sulphides of Pb, Sn, As, and Sb are more or less oxidized to $PbSO_4$, $SnO(OH)_2$, As_2O_5 (or H_3AsO_4), and Sb_2O_5, especially when conc. HNO_3 is used.

Hydrogen sulphide is prepared by acting on FeS with dilute HClAq or H_2SO_4Aq, the solution by passing the gas into cold water, previously boiled. From *acid* solutions H_2S precipitates only Ag, Hg, Pb, Cu, Cd, Bi, Sn, Sb, As as sulphides. From neutral or slightly alkaline solutions, or solutions of acetates, it also precipitates Co, Ni, Zn, Mn, and Fe more or less completely; from strongly alkaline solutions As, Sb, and Sn are not thrown down. For solubility of sulphides see under ammonium sulphide. H_2S and $(NH_4)_2S$ react with suspended precipitates, hydroxides, basic salts, etc., as well as solutions.

H_2S is very rarely used as a reducing agent in analytical work: it precipitates the sulphides by metathetical reactions, setting acid free.

$$M''R'_2Aq + H_2SAq = MS + 2HRAq$$

but some strong oxidizing agents are reduced by it with precipitation of S and removal of O or some acid radical to form H_2O or free acid:

$$2FeCl_3Aq + H_2SAq = 2FeCl_2Aq + 2HClAq + S$$

$$K_2Cr_2O_7Aq + 8HClAq + 3H_2S = 2KClAq + 2CrCl_3Aq + 7H_2O + 3S$$

141 *Sodium phosphate* precipitates all metals but the alkali group and As as phosphates, soluble in acids.

Potassium cyanide precipitates most of the heavy metals (except Hg″ and As) as cyanides, many of them dissolving in excess as double cyanides (especially Ag, Cu, Cd, Zn, Ni, Co, Fe″) some of which are reprecipitated on neutralization. See also 146.

Potassium ferrocyanide precipitates most of the heavy metals from slightly acid solutions: the ferrocyanides of Fe (blue), Cu (brown), U (brown), Zn (white), Ag (white), are characteristic; all are decomposed by KOH, reforming K_4FeCy_6.

Soluble chlorides, as HCl, precipitate Ag, Hg from mercurous salts (and Pb from strong solutions).

Soluble sulphates precipitate Ba, Sr, Pb (and Ca from strong solutions).

142 *Ammonium chloride* forms double chlorides with certain metallic radicals (especially Mg, Mn, Cu, Cd, Ni, Co, Fe″) and prevents their precipitation by NH_4OH. When ammonia is added to solutions of chlorides a certain amount of NH_4Cl is formed, and still more when free HCl is originally present.

It is also used occasionally to convert into chloride the metal of a fixed alkali (KOH into KCl) or the K in salts of weak acids. See 138.

Ammonium acetate is sometimes added when it is desirable to remove free HCl or other strong acid and replace it by acetic, without neutralizing the solution: or to convert other salts into acetates:

$$HClAq + NH_4(C_2H_3O_2)Aq = H(C_2H_3O_2)Aq + NH_4ClAq$$

$$FeCl_3Aq + 3(NH_4)(C_2H_3O_2)Aq = Fe(C_2H_3O_2)_3Aq + 3NH_4ClAq$$

It is also used to precipitate Al, Cr, and Fe‴, as on boiling their acetates are decomposed, precipitating basic acetates or hydroxides, which remain insoluble as long as liquid is hot:

$$2Fe(C_2H_3O_2)_3Aq + 3H_2O = 2Fe(OH)_3 + 6HC_2H_3O_2Aq$$

BLOWPIPE TESTS.

143 Tests made "in the dry way" are very useful in the preliminary analysis of solid substances, being rapidly performed and requiring but small quantities of material.

A convenient pattern of blowpipe is that known as Black's (Fig. 1); it should have a mouthpiece of wood or rubber and a nozzle made to screw on.

The blowpipe is used with a *luminous* flame about 4 cm. or 1½ inches high, such as that of an oil lamp, candle, or Bunsen burner with air holes closed. Some practice is necessary in order to keep up a continuous and uniform blast.

144 The *oxidizing flame* (O.F. see Fig. 2) is produced by holding the blowpipe nozzle very near the burner and well into the edge of the flame; on blowing gently a blue non-luminous cone is produced; the hottest point (H) is just outside the tip of this inner blue portion, and all beyond this (as at O) is *oxidizing*, its effects being due to the heated oxygen of the atmosphere.

The *reducing flame* (R.F. see Fig. 3) is formed by holding the nozzle a little higher and just at edge of flame; all within the blue cone is *reducing*, owing to the presence of unoxidized C and H compounds derived from the fuel.

145 *Borax beads* are made by taking up a little borax ($Na_2B_4O_7$ 10aq) in a *circular* loop (Fig. 4) ⅛ inch in diameter, at end of a platinum wire, and heating till it fuses to a clear glass; a little of the powdered material to be examined is then taken up and heat is again applied. Fused borax dissolves most metallic oxides and is colored by some, the colors in O.F. and R.F. frequently differing.

Beads of *sodium metaphosphate* ($NaPO_3$) are formed in the same way by heating microcosmic salt ($NaNH_4HPO_4$4aq) which loses water and ammonia. These are much more fluid than borax beads, they must be held at first as shown in Fig. 5, so that the salt is heated rather than the wire.

146 *Tests on charcoal* are made with a slip of coal sawn about an inch wide. The assay is placed in a shallow cavity near one end and the flame directed upon it while held in an inclined position; in the O.F. many substances form *sublimates* on the face (S, Fig. 6), usually consisting of oxides, the distance from the assay being a measure of the volatility; in R.F. many oxides and oxysalts are also reduced to metal, some more readily if mixed with Na_2CO_3 or KCN.

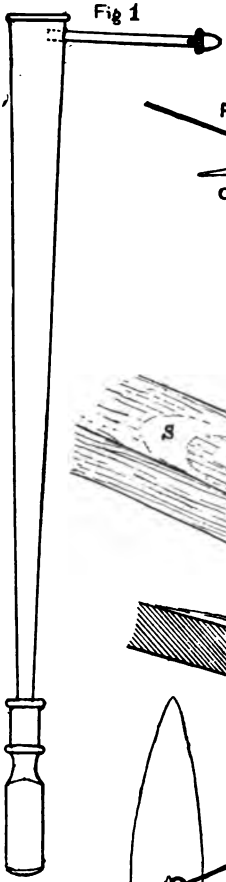

Fig 1

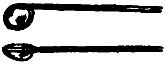

Fig 4

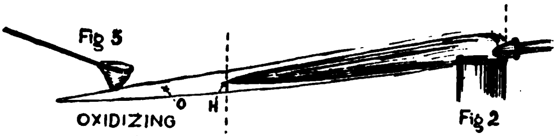

Fig 5

Fig 2

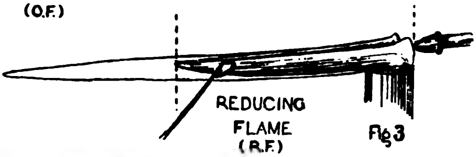

Fig 3

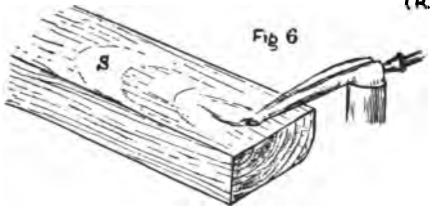

Fig 6

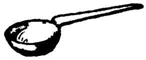

Fig 8

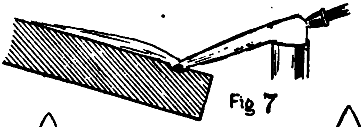

Fig 7

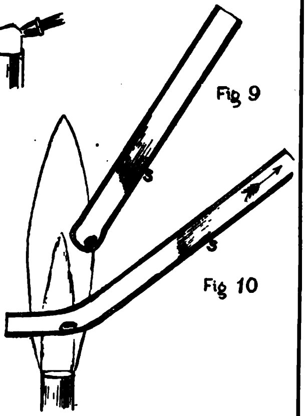

Fig 9

Fig 10

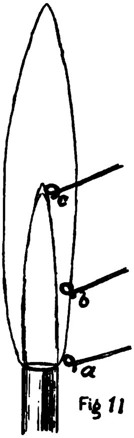

Fig 11

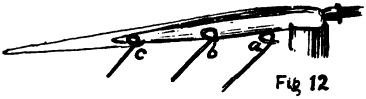

Fig 12

W.J.S. 189,

The coal is used primarily to give an infusible non-conductive support for the assay, the carbon acts also as a reducing agent forming CO or CO_2 with the oxygen of oxides. It does not reduce sulphides or chlorides until these have been fused with Na_2CO_3, which reacts with other salts forming carbonates, which usually lose CO_2 forming oxides, many of these being finally reducible by the heated charcoal or the gases of the reducing flame. Thus, there being an excess of Na_2CO_3:

$$PbS + Na_2CO_3 = Na_2S + PbCO_3 = Na_2S + PbO + CO_2,$$

$$2PbO + C = CO_2 + 2Pb$$

Fused KCN reduces sulphides and oxides, forming KCNS or KCNO.

$$PbS + KCN = KCNS + Pb$$

$$PbO + KCN = KCNO + Pb$$

Many sulphides are reduced by charcoal without fluxes, if first "roasted" by the O.F. to oxides.

$$CuS + 3O = SO_2 + CuO$$

The surface of the coal must be cleaned carefully before a second use.

147 *Fusions on platinum* are made in a spoon (Fig. 8) or piece of thin foil held in forceps, usually with Na_2CO_3 (or the more fusible $NaKCO_3$) and some oxidizing agent as $KClO_3$. Reducing agents must be avoided, as reduced metals injure the platinum. This alkaline flux converts compounds of acid-forming elements into salts of the alkali metals.

Potassium disulphate ($K_2S_2O_7$) is an acid flux, sometimes used to convert refractory metallic compounds into sulphates; it liberates SO_3 at a red heat, leaving K_2SO_4.

148 *Closed tubes* (Fig. 9) are made of moderately hard glass and should be about 3 inches long by $\frac{3}{16}$ in bore, closed at one end; if held aslant and heated volatile substances placed in them form sublimates, and decomposable ones may give off water or gases recognizable by various tests. They are easily made by taking a piece of tubing 6 inches long, heating the middle with the blowpipe flame, turning constantly till soft, drawing out, heating the end of each half and blowing to round the bottom.

Open tubes (Fig. 10) are slightly longer and wider, they are occasionally used to oxidize sulphides, etc., an up-current of heated air passing over the assay.

149 *Flame tests* are made by taking up a solid or strong solution on a platinum wire (previously cleaned by dipping in HClAq and igniting) and holding in a *colorless* Bunsen or blowpipe flame; some volatile substances then produce characteristic colors. By holding the wire first in the cooler portions of the flame (as at *a*, Figs. 11 and 12), and gradually moving it into the hotter portions (*b* and *c*), some idea of the volatility of the substance may be gained. Metallic chlorides are generally more volatile than oxides or other salts, hence flame colorations are best obtained after moistening with conc. HClAq. Some compounds require to be decomposed with hot conc. H_2SO_4 before making this test.

The wire used for flame colors is best kept distinct from that used for borax beads: each should be kept in HClAq when not in use.

150 SCHEME OF LABORATORY WORK.

After looking over the preceding pages perform (*a*) the preliminary exercises on the reactions of radicals (151) and separation (152), the latter includes the more important operations that will be met with. Then (*b*) work systematically through the *blowpipe tests* for the various metals (Part 2), using any of their solid compounds. Similarly (*c*) work through the reactions *in solution* of the metals of the silver group, using solutions of the nitrates. From the tabulated list of their reactions (212) draw up schemes by which these three radicals may be separated from one another, starting with a mixed solution of the three nitrates.

(*d*) Take a solution of the *nitrates* of the *silver group* metals, precipitate the chlorides and separate them by the method given in table for Precipitate I. Write all the equations involved.

(*e*) Take a second solution containing *chlorides* of all the metals of the *alkalis* and *alkaline earths:* treat with NH_4Cl,

NH_4OH, and $(NH_4)_2CO_3$, filter, and test precipitate and filtrate for the metals contained: see table III §V and §VI, and table IV for Pp V and VI.

(*f*) Take a third solution containing *chlorides* of all the metals of the *iron group:* prove presence of each, following table III §III and §IV, and table V for Pps III and IV.

(*g*) Similarly test a fourth mixture containing *nitrates* or *chlorides* of all the metals of the *copper* and *arsenic groups:* first converting them into sulphides by H_2S and treating the washed precipitate with $(NH_4)_2SAq$ or KOHAq: following table III §II and table VI.

In each case endeavor to ascertain the principles involved in the separations and the reasons for adding each reagent used: the notes at end of book should be consulted, and whenever a definite compound is formed, the equation corresponding to the reaction should be written. The typical equations in 137 to 142 will be of some assistance.

Whenever any doubt arises as to the identity of a precipitate confirm it by the tests given under the head of the respective metals in text, and compare with the effects of the same reagents on a known solution of the same metal.

(*h*) Work carefully through the reactions of the *acids*, applying the tests given in Part 3 to solid salts of these acids, or to solutions of their Na, K or (NH_4) salts.

(*k*) A number of *simple substances* (10 or 12) in the solid state should then be tested and their composition determined by blowpipe methods, the effect of water and acids (see table II); followed by a similar number of simple substances in solution (see tables I and II), the metal and acid radical being determined in each.

(*m*) Finally, a number of *complex mixtures*, solids or solutions, will be given for determination of all the metals and acid radicals; all the indications should be confirmed by characteristic tests.

151 THE IDENTIFICATION OF A PARTICULAR SUBSTANCE.

Take a small crystal of copper sulphate: examine its form, color, etc.; observe how readily its powder is soluble in water. Heat a fragment in a closed tube. Take a clean glass plate, put on it a few drops each of saturated solutions of various cupric salts, *e.g.*, the sulphate, chloride, nitrate, acetate, and of any metallic sulphates—*e. g.*, those of Fe, Zn, Mg, (NH_4), Na. Leave them to evaporate for some time, examine crystals formed. Take *dilute* solutions of the same salts: to small portions (2 or 3 ccs) of each add NH_4OHAq little by little till the mixture smells strongly; to other portions add $BaCl_2Aq$, followed by HClAq, and $Pb(C_2H_3O_2)_2Aq$ followed by HNO_3; to others, HClAq + H_2SAq, K_4FeCy_6Aq or any of the reagents mentioned in (217).

It will be observed that certain effects, *e. g.*, the brown precipitate with ferrocyanides, and the blue solution with ammonia, are always observed when the radical *Cu''* is present; others, as the white precipitates with Ba and Pb salts, are only seen when a *sulphate* is present. The reactions of the metallic radical in cupric salts are independent of the nature of the acid radical combined with it, and those of the acid radical in solutions of sulphates are the same, whatever metal may be present; the same is true of nearly all salts, so that in general it is possible to test for the metallic radicals and acid radicals independently. If, however, a metal forms part of an acid radical its reactions are frequently modified, *e. g.*, to a little $CuSO_4Aq$ add KCNAq till the precipitate redissolves to a clear liquid: it now contains $K_2(CuCy_4)$ or a similar compound: test portions of this solution with NH_4OH, H_2S, or K_4FeCy_6: the changed behavior is due to the Cu being now a part of the *acid radical:* by acidulating the solution with H_2SO_4 the copper again forms $CuSO_4$, which reacts as before.

EXERCISE IN MANIPULATION.

The powder supplied contains basic bismuth carbonate $(BiO)_2CO_3 \cdot \frac{1}{2}aq.$, secondary potassium arsenite K_2HAsO_3, potassium chromium sulphate $KCr(SO_4)_2 \cdot 12aq.$ Separate its constituent metals, following the directions given below, and write all the equations involved.

Dissolve: place about ¼ gram of it in a test tube, add 3 or 4 ccs distilled water, heat to boiling, holding tube in a holder of folded paper in an inclined position, it partially dissolves. Add 2 or 3 ccs dilute HClAq, warm gently for a few minutes, if not quite clear add more acid and heat again. *Precipitate the As and Bi:* to the hot solution add H_2SAq *in excess* (that is till solution after being warmed, shaken and allowed to stand a minute, smells distinctly of H_2S), transfer to a small beaker if necessary, continue heating, let precipitate settle somewhat and *filter.* Fold a circular filter paper, about 10 cm. in diameter, to a quadrant, open to a cone of 60° angle, place in a funnel somewhat larger than paper and moisten with wash bottle, beginning at edge. *Decant* the clearer part of liquid (by pouring it down a glass rod held against lip of test tube) upon middle of filter, which should never be over ¾ full. Test a portion of the filtrate with a little H_2SAq, if a precipitate forms the whole must be treated again with H_2S till precipitation is complete and again filtered. When nearly all liquid has passed through throw the bulk of precipitate on filter and rinse out tube, throwing rinsings on filter.

PRECIPITATE As_2S_3, Bi_2S_3.

* *Wash on filter* with a fine jet of water, driving to point of filter; when ⅓ full allow to drain completely; repeat washing, add first washings to main filtrate, neglect the rest. Two or three washings remove the soluble matter sufficiently for most qualitative purposes. *Transfer to test tube;* make a hole in point of filter with sharp-pointed glass rod, wash precipitate through into a test tube with a jet of water. Allow to settle, decant off as much water as possible from precipitate. *Digest with ammonium sulphide:* add

FILTRATE OR SOLUTION contains Cr and K as sulphate or chloride with HCl and H_2S. Heat to expel H_2S, evaporate to one-half bulk. Add a little NH_4ClAq, then NH_4OH in slight excess, i. e., till liquid smells of it and is strongly alkaline to litmus. Shake well, heat to boiling, filter hot.

PRECIPITATE $Cr(OH)_3$

FILTRATE contains K and NH_4 as chloride, sulphate or hydroxide. Place in dish, *evap-*

<table>
<tr>
<td colspan="3">5 ccs $(NH_4)_2SAq$, digest at moderate heat for 5 minutes, *i. e.*, heat to about 60°C (as hot as hand can bear) and stand in a beaker containing a little hot water, shaking or stirring occasionally. Allow to settle, decant clear solution upon a filter, wash residue once by decantation and finally on filter.</td>
<td rowspan="3">Wash; dry. Place on platinum foil with a little Na_2CO_3 and a pinch of $KClO_3$. Fuse at red heat. Yellow color of fused mass is due to $Na_2Cr^{vi}O_4$</td>
<td rowspan="3">*orate to dryness;* finish over a small flame or on sand bath; should spirting occur cover with inverted funnel till it ceases. Free NH_3 volatilizes with the water. When quite dry raise temperature cautiously and *ignite residue* by heating to low redness, under hood. NH_4Cl sublimes with other ammonium salts, K salts remain. Allow to become quite cold, dissolve in a few drops of water, dip a clean platinum wire in solution and heat in Bunsen flame. Purplish color (red violet through blue glass) shows presence of K; yellow color is due to Na.</td>
</tr>
<tr>
<td rowspan="2">RESIDUE
Bi_2S_3. Wash; dry the filter. Place Bi_2S_3 in a small hollow in a piece of charcoal. Heat in outer flame of blowpipe.
Yellow sublimate (Bi_2O_3) and brittle beads of metal indicate Bi.</td>
<td colspan="2">SOLUTION
contains $(NH_4)_4As_2S_5$ or $2(NH_4)_2S$ As_2S_3, a soluble ammonium thioarsenite. Test its reaction with litmus paper. Add HCl cautiously till acid, H_2S escapes. Heat to boiling, allow to settle. Filter. Wash.</td>
</tr>
<tr>
<td>PRECIPITATE As_2S_3.
Dry; place in small tube closed at one end, heat. As_2S_3 *sublimes.*</td>
<td>Filtrate HCl and NH_4Cl neglect.</td>
</tr>
</table>

The above separation is based upon the solubility in dilute HClAq of all the substances present, though the carbonate of Bi is insoluble in water: the insolubility of the sulphides of Bi and As in HClAq, while those of Cr and K do not form in acid solutions: the insolubility of Bi_2S_3 in alkaline solutions while As_2S_3 readily dissolves: the insolubility of $Cr(OH)_3$ in water or ammonia, potassium salts being soluble: and the volatility of ammonium salts at moderately high temperatures, K salts being much less volatile. The confirmatory tests are based on Bi_2S_3 being oxidized to Bi_2O_3 when heated in air, the oxide again being readily reduced to metal by heated carbon: upon As_2S_3 being yellow and volatile: on the fact that Cr has a tendency to form a higher oxide when heated strongly in presence of alkalis, this oxide being acidic and yielding strongly colored salts: and that potassium salts, when volatilized, give out light of a violet color.

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*It may be demonstrated that the washing of a precipitate is most effective when it is treated with a number of small additions of water, each being allowed to drain off before another is added.

PART II.

REACTIONS OF COMPOUNDS OF THE METALS.

201 These are studied in the order in which they are usually precipitated in the examination of complex substances, that is, they are grouped according to the solubility of their chlorides, sulphides, hydroxides and carbonates in water, acids and ammoniacal solutions. See Table I accompanying this book.

The less positive metals fall in the two groups first precipitated, the most positive in the last group, but there is no strict agreement between the grouping and the electro-positive character, or the periodic arrangement.

The metals are often classified as *alkali metals* (Na, K, Li, Rb, Cs), *metals of the alkaline earths* (Ba, Sr, Ca, Mg), and *heavy metals*, including all others: the latter are all precipitated from solution by ammonium sulphide (140), but a distinction may be made between heavy metals proper, which are precipitated as sulphides, and metals of the earths (*e. g.*, Al and Cr) which are precipitated by ammonium sulphide as hydroxides, and which do not form sulphides in the wet way.

It should be noted that there is no sharp natural distinction between metals and non-metals, some elements (*e. g.*, Te, Se, As, H) being assignable to one class by virtue of certain properties, and to the other by others.

In cases where so-called metallic elements also form acids the behavior of the latter is studied with that of the metallic radicals, and when a metal forms two or more classes of salts they are studied together unless they fall in separate groups in analysis, as is the case with the salts of iron and mercury.

In systematically studying the reactions in solution some salt of one of the stronger acids should be used, preferably the chloride or nitrate, as these are the forms in which the metals usually occur in the solutions obtained in actual analyses: for the blowpipe tests almost any solid compound may be used, such as one of the precipitates obtained in working with the solutions.

The symbols in italics indicate reagents, generally in water solution, added to the solutions under examination.

METALS PRECIPITATED FROM ACID SOLUTIONS BY HYDROGEN SULPHIDE.

202 These form the Silver, Copper, and Arsenic groups, and include the less positive metals. Soluble salts of all these metals with strong acids redden litmus: most of them are easily reduced from their compounds.

SILVER GROUP.

Pb, Ag, Hg′ in mercurous salts.

203 The chlorides of the metals of this group are white and insoluble or difficultly soluble in water; the bromides, iodides and sulphates are difficultly soluble. The sulphides are black and insoluble in solutions of alkaline sulphides or hydroxides and in dilute acids. Their solutions are easily reduced, *e. g.*, by metallic zinc, in the order Ag, Hg, Pb, and their solid compounds by heating with Na_2CO_3 and charcoal.

LEAD: Pb″

204 BLOWPIPE TESTS: Heated on charcoal with Na_2CO_3 in inner flame all compounds yield beads of metal, malleable and so soft as to mark paper, the metal is oxidized* by outer flame. A sublimate of oxide forms rather near assay, orange to yellow while hot, yellow to white cold, volatile, can be driven about by flame which is colored blue (compare Bi). The oxide and most oxysalts are reducible without fluxes.

**Cupellation:* If a few grams of powdered bone-ash are compressed into a hollow in charcoal, and a piece of metallic lead is placed in a slight cavity in the heated bone-ash and kept covered by an oxidizing flame it is gradually oxidized and the fused PbO absorbed: any non-oxidizable metals (Au, Ag, Pd, Pt) previously alloyed with the lead are left in the metallic state, others (Sn and Fe) leave infusible oxides, while others (Cu) are oxidized and carried off by the PbO, if the proportion of lead is large enough.

205 REACTIONS IN SOLUTION: for practice use $Pb(NO_3)_2Aq$.

HCl (or any soluble chloride) pps white $PbCl_2$, but incompletely and only from the stronger solutions, $PbCl_2$ being soluble in 130 parts of cold or 33 of boiling water, crystallizing out on cooling; NH_4OH converts it into $PbClOH$, which is insoluble even in hot water.

H_2S pps black PbS insoluble in alkalis or cold dilute acids, soluble in hot *dilute* HNO_3Aq as $Pb(NO_3)_2$, S separating; *conc.* HNO_3 oxidizes it to white insoluble $PbSO_4$. Conc. HClAq and H_2SO_4 convert it into *chloride or sulphate.* See also under Copper group (215).

H_2SO_4 (or any soluble sulphate) pps $PbSO_4$, insoluble in excess, ppd completely on addition of alcohol, somewhat soluble in dilute HClAq or HNO_3Aq, soluble in KOHAq as K_2PbO_2 (plumbite), and in $NH_4C_2H_3O_2Aq$ forming a double acetate. Pp is decomposed by hot Na_2CO_3Aq.

KOH pps white $Pb(OH)_2$ or basic salt, soluble in excess as K_2PbO_2.

NH_4OH pps white basic salt, insoluble in excess, but no pp is usually obtained from the acetate.

Na_2CO_3 pps white basic carbonate, insoluble in KCNAq.

$K_2Cr_2O_7$ pps yellow $PbCrO_4$, soluble in KOHAq, insoluble in acetic acid and in very dilute HNO_3Aq.

KI pps yellow PbI_2, soluble in hot water or in conc. KIAq.

Many other reagents give pps from solutions of lead salts often with colors characteristic of the acid radicals,* but nearly all lead compounds (except PbS) are soluble in an excess of KOHAq, and most of them in HNO_3Aq, but not in KCNAq.

PLUMBITES (*e. g.*, K_2PbO_2), derived from the anhydride PbO, occur in alkaline solutions, as when $Pb(OH)_2$ and lead salts are treated with KOHAq, they are decomposed on neutralization. PLUMBATES are derived from the anhydride PbO_2, and are decomposed by HClAq with evolution of Cl.

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* See reactions of the acids in Part 3.

SILVER: Ag′.

206 BLOWPIPE TESTS: for practice use any solid compound, as Ag_2S or any of the precipitates obtained by the reagents in 207.

Heated on charcoal with Na_2CO_3 all compounds yield beads of white metal, difficultly fusible and not oxidizable. Most compounds are reduced on charcoal without flux.

207 REACTIONS IN SOLUTION: for practice use $AgNO_3Aq$.

HCl (or any soluble chloride) pps white curdy AgCl, darkened by sunlight, fused by strong heating; insoluble in acids unless added in great excess, soluble in NH_4OHAq (as $AgCl(NH_3)_xAq$), and in KCNAq (as $KAgCy_2$) reppd by acidulating with HNO_3; soluble in $Na_2S_2O_3Aq$ (as $Na_4Ag_2(S_2O_3)_3$) and slightly in solutions of chlorides (NaCl, etc.)

H_2S pps black Ag_2S, insoluble in alkalis or acids, except hot HNO_3 (140), difficultly soluble in KCNAq.

$(NH_4)_2S$ pps also Ag_2S, insoluble in excess.

KOH pps brown Ag_2O, insoluble in excess, soluble in NH_4OHAq.

NH_4OH pps Ag_2O, very readily soluble in excess (as NH_4AgO), and in some ammonium salts: no pp forms in weak solutions.

KCN pps white AgCN, soluble in excess or in NH_4OHAq, reppd by acidulation: pp is decomposed by hot conc. HNO_3 or by strong heating, otherwise is like AgCl.

Metallic copper and most other metals pp metallic silver; many other reducing agents, as gaseous PH_3 and AsH_3, pp Ag; Hg reduces Ag forming an amalgam.

Precipitates are thrown down from silver solutions by many other reagents, but all of them dissolve in KCNAq (as $KAgCy_2$) and most of them either in NH_4OHAq or in HNO_3Aq, the colors and solubilities affording distinctive tests for the acid radicals.* These are reprecipitated from the ammoniacal and cyanide solutions, usually in the same form, by acidulation with HNO_3.

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*See reactions of the acids in Part 3.

MERCURY: Hg′ or Hg″.

208 Blowpipe Tests (tests applicable to either mercurous or mercuric compounds): use any solid compound. Heated in closed tubes all mercury compounds either sublime unchanged (*e. g.*, HgCl, $HgCl_2$, HgS) or are decomposed (*e. g.*, HgO and oxysalts) yielding a mirror-like sublimate of metal. Heated with dry Na_2CO_3 in closed tubes all compounds give a silvery mirror or globules of metal. Heated on charcoal all give remote and extremely volatile sublimates.

209 Reactions in Solution: applicable to any solution,

Metallic copper, in presence of free acid, becomes gradually coated with silvery metal, which is removed by gentle heating.

Zinc, and most other metals, become gradually amalgamated.

$SnCl_2$, in excess, gives a gray precipitate of metal.

N. B. All the mercury precipitates (210, 214) are soluble in *aqua regia*.

MERCUROUS SALTS: Hg′. Compare 213.

210 Reactions in Solution: use $Hg'NO_3$ dissolved in dilute HNO_3Aq.

Water, added in excess, partially pps white basic salts (*e. g.*, $Hg_2O.2HgNO_3$) unless a fair proportion of free acid is present.

HCl (or a soluble chloride) pps white HgCl, insoluble in dilute acids, except hot HNO_3Aq or aqua regia, slightly soluble in boiling HClAq (forming soluble Hg″ salts): NH_4OH blackens pp forming insoluble $NH_2Hg'_2Cl$ or Hg + $NH_2Hg''Cl$.

KOH pps black Hg_2O, insoluble in excess.

NH_4OH pps black mercurosammonium compounds.

H_2S pps black Hg_2S (= Hg + HgS) insoluble in dilute acids, even hot HNO_3Aq; hot conc. HNO_3 yields a white insoluble sulpho-nitrate.

$(NH_4)_2S$ gives the same pp, insoluble in excess.

$K_2Cr_2O_7$ pps orange Hg_2CrO_4 or a basic chromate.

$SnCl_2$ pps gray metallic Hg mixed with HgCl, an excess reduces it completely on warming.

Oxidizing agents, Cl or Br, conc. HNO_3, or aqua regia oxidize mercurous to mercuric compounds (see 214).

211 The rare metal THALLIUM is precipitated from Thallous salts (Tl′) by HCl as TlCl: it is best recognized by the intense green flame coloration or the characteristic green spectroscopic line.

212 Separation of the Metals of the Silver Group.

Tabular comparison of reactions

	Pb	Ag	Hg′
HCl, with solutions	White pp	White pp	White pp
+ NH_4OHAq	insoluble	soluble	blackened, insol.
+ KOHAq	soluble.	insol.	blackened, insol.
KOHAq	white pp	brown pp	black pp
in excess	soluble	insol.	insol.
NH_4OHAq	white pp	brown pp	black pp
in excess	insol.	soluble	insol.
H_2SO_4 added to dilute solutions	white pp	no pp	no pp
H_2S	black pp	black pp	black pp
Heated on charcoal with Na_2CO_3	Red. to metal oxidized by O.F.	Red. to metal not oxidized	Volatilized

From this list it is evident that several schemes may be devised for separating these metals from one another, starting with a solution of the nitrates. Draw up as many such schemes as seem possible, using this list and any other available data.

Take a solution containing all these metals (about 10 ccs of a solution of about ¼ % of each is convenient) precipitate by HClAq and separate them, following directions in tables II and IV. Then separate them in another portion by one of the other systems devised.

COPPER GROUP.

Hg″, Pb, Cu, Cd, Bi.

213 Hydrogen sulphide precipitates all the metals of this group as sulphides, insoluble in dilute acids. Alkaline carbonates precipitate them as carbonates, usually basic, and sodium phosphate as normal phosphates.

210**214** MERCURIC SALTS: Hg″. See 208, 209, and compare 210.

Reactions in Solution: Use $HgCl_2Aq$, or $Hg(NO_3)_2$ in dilute HNO_3Aq.

HCl gives no pp.

Water, added in excess, partially pps the nitrate and oxy-salts, as white basic salts or yellowish HgO, unless a fair proportion of free acid is present, but does not affect $HgCl_2$.

KOH or *Na_2CO_3* pps brown basic salt or yellow HgO; insoluble in excess.

NH_4OH pps white mercuric-ammonium salt; insoluble in excess; soluble in HClAq.

H_2S gives a pp, *white at first* (Hg_2SCl_2, etc.) which with more H_2S becomes yellow, brown and finally *black* HgS; insoluble in acids, even in boiling HNO_3Aq (conc. HNO_3 slowly forms white insoluble $Hg_3S_2(NO_3)_2$); insoluble in NH_4OHAq or $(NH_4)_2SAq$; somewhat soluble in $Na_2SAq+NaOHAq$; *soluble in aqua regia.*

$(NH_4)_2S$ gives the same white pp, finally black HgS; insoluble in excess.

KI pps orange or red HgI_2; soluble in excess.

$SnCl_2$ pps white HgCl at first; larger quantities reduce this completely to gray metallic Hg.

Mercuric solutions are highly corrosive, attacking many metals (*e. g.*, Ag, Fe) and being reduced to mercurous salts or to metal (see 210).

215 LEAD: Pb″. See also under Silver Group.

Lead chloride is somewhat soluble in water, hence some lead always remains in solution after the silver group is precipitated.

H_2S pps black PbS; if it is added in excess to a sufficiently dilute solution the precipitation is complete; presence of much free acid tends to retain it in solution. In presence of much free HCl a brick-red pp of sulpho-chloride (*e. g.*, Pb_2SCl_2) may form, converted into PbS by an excess of H_2S. If not completely removed by H_2S Pb is very apt to be mistaken for metals in other groups.

COPPER: CUPRIC SALTS: Cu″.

216 Blowpipe Tests: use $CuSO_4$ or CuO.

Flame is colored a vivid blue-green by compounds moistened with HClAq: green in absence of Cl. Borax bead in O.F. is green hot and bluish cold, in R.F. opaque red on cooling if much Cu is present, forming Cu_2O. Heated on charcoal in R. F. with Na_2CO_3 compounds are reduced to red metal, difficultly fusible; oxysalts are reduced without flux.

217 Reactions in Solution: use $CuSO_4Aq$.

Crystallized salts and solutions are generally blue or green.

KOH pps bluish $Cu(OH)_2$, insoluble in excess, except in presence of organic matter; soluble in NH_4OHAq (blue) and in KCNAq (colorless); on heating the pp is converted into black CuO.

NH_4OH pps bluish basic salt, soluble in excess (azure blue) as $CuSO_44NH_3Aq$; KCN removes this color. H_2S added to blue solution pps black CuS, but does not affect the colorless double cyanide.

H_2S pps brownish black CuS, insoluble in dilute HClAq or H_2SO_4Aq; soluble in hot dilute HNO_3Aq and in KCNAq.

$(NH_4)_2S$ pps CuS, slightly soluble in excess, especially of the yellow salt, reppd by acids, liver-colored.

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Na_2CO_3 pps greenish basic carbonate $\mathrm{Cu_2(OH)_2CO_3}$, black CuO on boiling, soluble in KCNAq.

K_4FeCy_6 pps brownish $\mathrm{Cu_2FeCy_6}$ or $\mathrm{K_2CuFeCy_6}$, insoluble in acetic acid, decomposed by KOH.

Bright metallic iron reduces red metallic Cu and is plated by it; *Zinc* pps it, sometimes in a black form; *Aluminium* reduces Cu readily in presence of a chloride or from a hot solution: if platinum is placed in contact with either of these metals the ppd Cu is deposited on it.

All the precipitated copper compounds are soluble in KCNAq as double cyanide ($\mathrm{K_2CuCy_4}$, etc.) and most, except CuS, in ammonia and in dilute $\mathrm{HNO_3}$Aq.

218 Cuprous salts are rarely met with, and readily oxidize to cupric, acting as strong reducing agents: most are difficultly soluble in water: CuCl is white.

CADMIUM: Cd″.

219 Blowpipe Test: on charcoal in R.F. compounds give a brown sublimate, very volatile and transient, the flame being momentarily colored brown.

220 Reactions in Solution: use $\mathrm{Cd(NO_3)_2}$Aq or $\mathrm{CdCl_2}$Aq.

KOH pps white $\mathrm{Cd(OH)_2}$; insoluble in excess.

NH_4OH pps white $\mathrm{Cd(OH)_2}$, soluble in excess, soluble in KCNAq as $\mathrm{K_2CdCy_4}$. $\mathrm{H_2S}$ pps these alkaline solutions (compare Cu).

H_2S pps yellow finely pulverulent CdS, which tends to pass through filter; insoluble in *very* dilute acids; soluble on warming and in $\mathrm{H_2SO_4}$Aq; insoluble in alkalis, alkaline sulphides and in KCNAq.

$(NH_4)_2S$ pps CdS; insoluble in excess.

Na_2CO_3 pps white $\mathrm{CdCO_3}$; soluble in KCNAq.

Nearly all Cd precipitates, except CdS, dissolve readily in KCNAq as $\mathrm{K_2CdCy_4}$.

BISMUTH: Bi'''. Compare Pb (204) and Sb (234).

221 BLOWPIPE TESTS: heated on charcoal Bi compounds are very easily reduced to fusible beads of *brittle* metal; giving a sublimate (Bi_2O_3) yellow to brown hot, white to yellow cold; volatile, exactly like that of PbO, but without coloring flame. Addition of flux is rarely necessary. The metal can be cupelled like Pb.

222 REACTIONS IN SOLUTION: use $Bi(NO_3)_3$ dissolved in dilute HNO_3Aq. Bismuth salts are only completely soluble in water when free acid is present.

Water, in excess, incompletely pps white basic salts, or salts of the radical bismuthyl BiO (*e. g.*, $BiONO_3$), from solutions which do not contain too much free acid. The oxychloride, or bismuthyl chloride (BiOCl), is one of the least soluble of these, hence the addition of a *little* HCl facilitates precipitation. The basic salts dissolve in HClAq or HNO_3Aq, not readily in tartaric acid (compare Sb).

KOH or NH_4OH pps white BiOHO, becoming yellow; insoluble in excess, soluble in dilute HClAq.

H_2S pps brown-black Bi_2S_3; insoluble in dilute acids, alkalis or KCNAq; soluble in hot dilute HNO_3Aq.

$(NH_4)_2S$ pps Bi_2S_3, insoluble in excess.

$Sn''Cl_2$ + *excess of KOH* ($= K_2Sn''O_2 + KOH$) reduces black Bi_2O_2, $K_2Sn^{IV}O_3$ being formed.

$K_2Cr_2O_7$ pps yellow basic chromate $Bi_2O(CrO_4)_2$, soluble in acids, *insoluble in KOHAq:* compare Pb.

Na_2CO_3 pps white $(BiO)_2CO_3$, insoluble in KCNAq.

Bismuth precipitates are insoluble in alkaline solutions.

Rarer Metals of the Copper Group.

223 PALLADIUM, RHODIUM, RUTHENIUM and OSMIUM are met with as native elements alloyed or associated with Au, Pt and Ir. Pd resembles Ag but is less fusible and is difficultly soluble in acids, except aqua regia, attacked by fused $HKSO_4$: with KIAq its solutions (*e. g.*, $PdCl_2$) give a black pp of PdI_2. The others are infusible in the blowpipe flame, but Os is oxidized by the outer flame or by HNO_3 to volatile OsO_4 with an odor like Cl. Rh is attacked by fused $HKSO_4$ giving a reddish soluble double sulphate. Ru and the alloy of Os + Ir are very little affected by aqua regia. The solutions of the chlorides are reduced to metal by zinc and aluminium: and the solid compounds (except those of Os) by heat.

Separation of the Metals of the Copper Group.

224 The copper, silver, and arsenic groups are coprecipitated as sulphides by addition of H_2S to an acid solution. A fair proportion of free acid insures the non-precipitation of the iron group metals. A prior treatment with HCl removes the silver group as chlorides, and a subsequent treatment of the precipitated sulphides with $(NH_4)_2SAq$, KOHAq or Na_2SAq removes the arsenic group as thio-salts, together with a portion of the HgS or CuS, leaving the metals of the copper group as sulphides. From the mixed sulphides HgS is always first removed by its insolubility in hot HNO_3Aq: Bi and Pb are then separated from Cu and Cd by the insolubility of the former carbonates in KCNAq or of the hydroxides in NH_4OHAq; the differences in solubility of the sulphates of Bi and Pb in H_2SO_4Aq, and of the sulphides of Cu and Cd in KCNAq or H_2SO_4Aq, complete the separation.

ARSENIC GROUP.

As, Sb, Sn.

225 These are all capable of two degrees of oxidation. They are the least positive of the metals, As having most of the characteristics of a non-metal, it and Sb forming gaseous hydrides. The oxides of As and Sb act as acids in nearly all cases, that of Sn frequently. All form chlorides, but not carbonates, and few salts with the weaker acids As and Sb form no nitrates, and As no sulphate. The chlorides have an acid reaction and are decomposed on addition of water. Their salts with alkali metals have an alkaline reaction.

H_2S precipitates the acid, but not the strongly alkaline solutions. The group is distinguished by the ready solubility of the sulphides and hydroxides in yellow ammonium sulphide and in potassium or sodium sulphide, as well as in caustic potash or soda solutions.

ARSENIC: As''' and As^{v}.

226 BLOWPIPE TESTS: heated in closed tubes As and most compounds readily volatilize giving sublimates: *e. g.*, As_2O_3 white, As_2S_3 orange, As gray. If previously mixed with dry Na_2CO_3 and C they give steel gray mirrors of metallic As: the oxides are reduced by C alone.

On charcoal in the R.F. all yield a remote white sublimate of As_2O_3—very volatile—and a characteristic garlic odor: the flame is at the same time colored bluish.

227 REACTIONS IN SOLUTION: applicable to all compounds soluble in HClAq: use As_2O_3Aq.

Reinsch's Tests: acidulate with HCl, insert a piece of bright copper wire, remove after an hour or two; gray As or Cu_5As_2 is reduced upon it. Dry thoroughly, place in small closed tube and heat, a white crystalline sublimate of As_2O_3 forms; with much, gray As may also sublime. With traces of As no sublimate may be obtained, but the copper is discolored by a very minute trace. Compare Sb (233).

Marsh's Test: formation of arsine. Bend a piece of glass tube (about 12 inches long x $\frac{3}{16}$), twice at right angles └───┐, make a moderately fine jet at one end and fit the other by a cork to a medium-sized test-tube or small (50 to 100 cc) flask.* In the latter put a few small pieces of zinc (purest obtainable) and add sulphuric acid, diluted about 1:5; when effervescence commences add a few ccs. of solution to be tested, adjust cork and *when air is expelled* light gas at jet. Hold a *cold, dry* evaporating dish so that its interior is *quite close* to jet; the AsH_3 is decomposed and a black *mirror-like* spot of As forms: if held at a distance some As_2O_3 is also formed and the spot has less lustre: the ppd metal is easily soluble in NaClOAq. The reaction is due to reduction of the As compound to AsH_3 by nascent H, while AsH_3 is decomposed by heat. Traces of As in wall paper, etc., can be found in this way. On heating the straight part of outlet tube a mirror-like ring of metal forms in it, which is not difficult to volatilize.

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*This apparatus should be kept for testing for As, as it serves to detect it in presence of all other metals. A blank test should be made first to prove whether As is contained in the zinc or acid used, it is rarely absent, but the faint spots thus obtained can be compared with those observed in the actual analysis. HClAq + Al or conc. NaOHAq + Al may also be used to generate the H requisite. For a detailed comparison of the distinctions between the As and Sb spots see Prescott and Johnson.

Formation of arsenic acid: if heated with HNO_3 As and all compounds form soluble H_3AsO_4: see two last tests in 230.

$Na_2S_2O_3$ pps yellow sulphide, forming Na_2SO_4.

228 ARSENIOUS SALTS: As‴.

Reactions in Solution: use $Na_2HAsO_3 + HClAq$, or $As_2O_3 + HClAq$, equivalent to solutions of $AsCl_3$.

N. B. Boiling a solution containing As‴ and free HCl volatilizes the As as $AsCl_3$.

From such acid solutions:

H_2S readily pps yellow As_2S_3, insoluble in dilute acids and in moderately conc. HClAq, soluble in HNO_3Aq and in aqua regia or ClAq as H_3AsO_4 (see 230), soluble in $(NH_4)_2SAq$ as thio-arsenite, in KOHAq, NH_4OHAq, Na_2CO_3Aq, $(NH_4)_2CO_3Aq$ and $NaHSO_3Aq$ as mixtures of arsenites and thio-arsenites, from which it is reprecipitated on acidulating with HCl: yellow $(NH_4)_2S_xAq$ it dissolves as thio-arsen*ate*, ppd by HCl as As_2S_5.

$(NH_4)_2S$ pps yellow As_2S_3, soluble in excess or in alkalis, reppd by acids.

None of the other group reagents give pps.

229 ARSENIC SALTS: As^{v}.

REACTIONS IN SOLUTION: use Na_2HAsO_4 + HClAq, or H_3AsO_4 + HClAq, equivalent to solutions of $AsCl_5$. From HClAq solutions As^{v} is not expelled by boiling.

From such *acid* solutions:

H_2S gives no pp at first, on heating to 70° C it slowly pps yellow As_2S_3 mixed with S (and As_2S_5): pp has the properties of As_2S_3 (228), but alkaline solutions contain thioarsen*ates*; precipitation is more complete if As^{v} is first reduced to As''' by SO_2Aq, and excess of SO_2 boiled off.

$(NH_4)_2S$ pps As_2S_3 + S, soluble in excess as thio-arsenate, reppd by HClAq as As_2S_5.

230 ARSENITES AND ARSENATES.

Most of these correspond to the ortho-arsenious and arsenic acids, $H_3As'''O_3$ and $H_3As^{v}O_4$, all are derived from the anhydrides As_2O_3 and As_2O_5. For practice use solutions of the secondary sodium salts Na_2HAsO_3 and Na_2HAsO_4.

REACTIONS IN SOLUTION.	ARSENITES.	ARSENATES.
$AgNO_3$ pps (from neutral* solutions only)	yellow Ag_3AsO_3	red-brown Ag_3AsO_4
$CuSO_4$ pps	green $CuHAsO_3$	blue-green $CuHAsO_4$
HCl pps from conc. sols. only	white As_2O_3	
H_2S from neutral or alk. sols.	no pp	no pp
H_2S + HCl pps	yellow As_2S_3 readily	yellow As_2S_3 + S slowly on heating
HNO_3 upon heating	oxidizes to H_3AsO_4 arsen*ic* acid	sets free H_3AsO_4
$(NH_4)_2MoO_4$ after acidulating with HNO_3 pps		yellow ammonium arseno-molybdate, insoluble in HNO_3Aq sol. in NH_4OHAq.
Magnesia mixture from solutions made alkaline with NH_4OH pps		white $Mg(NH_4)AsO_4$, insol. in NH_4OHAq, soluble in acids.

The two last reagents act in the same way with H_3AsO_4 as with H_3PO_4. $AgNO_3$ distinguishes them.

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* Solutions must be carefully *neutralized* by HNO_3Aq or NH_4OHAq, pps dissolve in an excess of either.

231 THIO-ARSENITES AND THIO-ARSENATES (derived from the acids $H_3As^{III}S_3$ and $H_3As^{V}S_4$) occur in the alkaline solutions formed by the action of alkaline sulphides (and also by hydroxides, carbonates, etc.) on As_2S_3 and As_2S_5. If free S is present, and with yellow polysulphides, the thio-arsen*ates* are always formed. On acidulating with HCl they yield yellow pps of As_2S_3 and As_2S_5, not easily distinguished, both soluble in NH_4HCO_3Aq or NH_4OHAq. Besides the normal K and NH_4 salts of the above ortho-acids others more complex are known; *e. g.*, $2(NH_4)_2S.As_2S_3$ or $(NH_4)_4As_2S_5$, and $2(NH_4)_2S.As_2S_5$ or $(NH_4)_4As_2S_7$. Those of heavy metals are insoluble.

ANTIMONY: Sb^{III} and Sb^{V}.

232 BLOWPIPE REACTIONS: heated on charcoal with Na_2CO_3 or KCN in R.F. Sb compounds are reduced to beads of gray, brittle, fusible metal, easily oxidized, forming a white sublimate of Sb_2O_3 at some distance from assay, volatile in O.F., coloring flame greenish. The fused bead, on removing flame, burns, forming crystals of oxide: if let fall on paper it leaves a black track. The white sublimate, or white compounds, moistened with $Co(NO_3)_2Aq$ and strongly heated in O.F. leaves a bluish-green mass. In the closed tube a few compounds yield sublimates ($SbCl_3$, Sb_2S_3).

233 REACTIONS IN SOLUTION: applicable to all soluble compounds.

Acidulation with HClAq, alone or followed by a large dilution with water, usually gives white pps of basic Sb^{III} chlorides or of Sb_2O_5, this effect being prevented by tartaric acid, pps are soluble in tartaric acid solution and in conc. HClAq.

Reinsch's test: see under As 227: Cu reduces Sb from HCl solutions as a black film, but this gives no sublimate when dried and heated.

Formation of Stibine (see 227): procedure as in Marsh's test for As: the Sb spots obtained by holding porcelain in flame of SbH_3 are sooty black: to further distinguish, treat spots with NaClOAq. As readily dissolves, Sb only slowly. Al + NaOHAq does not yield SbH_3.

Metallic zinc reduces black Sb from solutions containing a little free HCl; with large proportions of HCl much of the Sb passes off as SbH_3: if platinum is placed in contact with the zinc it is coated with brown or black Sb.

Salts of Bi and Cu give similar stains, but Sn, ppd in the same way, is gray, and coats the zinc rather than the platinum. Presence of HNO_3 interferes with the test.

HNO_3 converts the metal, sulphides, and compounds generally into white Sb_2O_3, nearly insoluble in water or dilute HNO_3Aq: on drying and heating to low redness this leaves SbO_2 or antimonious antimonate $Sb^{III}Sb^{V}O_4$.

234 ANTIMONIOUS SALTS: use a solution of $SbCl_3$ in HClAq or $SbOKC_4H_4O_6$Aq (tartar emetic or potassium antimonyl tartrate).

Dilution with water decomposes most antimonious solutions, especially the chloride, precipitating basic compounds (SbOCl, $Sb_4O_5Cl_2$, etc.): this is retarded by presence of a large proportion of acid, especially of tartaric acid (the tartrate is the only Sb^{III} salt not ppd by water), but a small addition of HCl before dilution facilitates pp. Sb^{III} tends to form basic salts, compounds of the radical (SbO) antimonyl, of which the tartrate is soluble in water.

KOH pps white Sb_2O_3, soluble in excess as K antimonite ($KSbO_2$, etc.) and in excess of HClAq: from acid solutions SbOCl, etc., often pp on first neutralization of the free acid.

NH_4OH pps Sb_2O_3, insoluble in excess.

Na_2CO_3 pps Sb_2O_3, soluble in excess on heating.

H_2S pps orange to red Sb_2S_3, insoluble in dilute, but soluble in hot moderately conc. HClAq; soluble in $(NH_4)_2SAq$ and K_2SAq as thio-antimonites, and in the yellow polysulphides as thioantimonates: HCl re-pps the former as Sb_2S_3, the latter as Sb_2S_5: soluble in KOHAq (and re-ppd by HCl) but not in $(NH_4)HCO_3Aq$ or $NaHSO_3Aq$. Warmed with a few drops of conc. HNO_3 pp oxidizes to insoluble Sb_2O_5 or $HSbO_3$.

$(NH_4)_2S$ pps Sb_2S_3, soluble in excess, re-ppd by HCl.

$Na_2S_2O_3$ pps Sb_2S_3 often mixed with S, forming Na_2SO_4.

235 ANTIMONIC SALTS: Sb^V.

REACTIONS IN SOLUTION: use $SbCl_5$ or Sb_2O_5 dissolved in HClAq.

H_2S pps Sb_2S_5, mixed with Sb_2S_3 and S, pp resembles Sb_2S_3 (234) in properties and color, dissolving in alkalis to form thio-antimonates, K_3SbS_4, etc., re-ppd by HCl as Sb_2S_5.

$(NH_4)_2S$ gives the same pp, soluble in excess.

KOH pps Sb_2O_5 or $HSbO_3$, soluble in excess of KOHAq as an antimonate.

NH_4OH gives the same pp, insoluble in excess.

KI liberates free I with Sb^V salts in HClAq solution (coloring CS_2, see 306), distinguishing Sb^V from Sb^{III}, which gives pps similar in appearance and properties.

236 ANTIMONITES AND ANTIMONATES, derived from the anhydrides Sb_2O_3 and Sb_2O_5, occur in the solutions of Sb compounds in KOHAq and NaOHAq, and some are known in the solid state. From these alkaline solutions *HCl*, on neutralization, pps the oxides, an excess redissolving them as $SbCl_3$ and $SbCl_5$: *KI* pps free I with antimonates, thus distinguishing them. Ortho-, pyro-, and met-antimonates are known, corresponding to the phosphates, but are not distinguishable by simple means: the formation of a pp of acid sodium pyroantimonate ($Na_2H_2Sb_2O_7.6aq$) is sometimes used as a test for Na.

237 THIOANTIMONITES AND THIOANTIMONATES are derived from Sb_2S_3 and Sb_2S_5 by addition of metallic sulphides, and occur in the solutions of these sulphides in alkaline sulphide solutions, and also in KOHAq or NaOHAq. These are ppd by acidulation yielding Sb_2S_3 and Sb_2S_5 respectively, the latter often mixed with free S and being usually the lighter in color, though the colors vary considerably with the conditions of precipitation.

TIN: Sn'' and Sn^{IV}.

238 BLOWPIPE TESTS: on charcoal, fused in R.F. with KCN all compounds yield small beads of fusible white metal and a coating close to assay, white cold, yellowish hot, non-volatile; moistened with $Co(NO_3)_2Aq$ and ignited this becomes bluish green.

STANNOUS SALTS: Sn''.

239 REACTIONS IN SOLUTION: use $SnCl_2 + HClAq$. All are strong reducing agents and in air become oxidized to stannic compounds, more rapidly by Cl or nitric acid.

The following reactions take place in solutions rendered slightly acid by HCl.

H_2S pps dark brown SnS; insoluble in dilute HClAq, NH_4OHAq, $(NH_4)_2CO_3Aq$, or colorless $(NH_4)_2SAq$; readily soluble in KOHAq or *yellow* $(NH_4)_2S_xAq$; reprecipitated on acidulating with HCl as SnS and SnS_2 respectively; soluble in moderately strong HClAq on heating.

$(NH_4)_2S$ pps SnS; soluble in excess of the *yellow* sulphide, as *thiostannate* $(NH_4)_2SnS_3$.

KOH pps white $Sn(OH)_2$; soluble in excess, as K stannite K_2SnO_2.

NH_4OH, *$(NH_4)_2CO_3$* or *Na_2CO_3*, pps white $Sn(OH)_2$; insoluble in excess.

$HgCl_2$ is precipitated as white HgCl or, if a small quantity is added, as gray Hg; $SnCl_4Aq$ is formed in either case.

Zinc pps gray metallic Sn; soluble in HClAq as $Sn''Cl_2$.

Copper does not reduce stannous salts.

Water, in excess, gives a milky basic pp, soluble in HClAq.

STANNIC SALTS: Sn^{IV}.

240 REACTIONS IN SOLUTION: use $SnCl_4$ + HClAq.
In solutions made slightly acid with HCl:

H_2S pps slowly (more readily on heating) yellow SnS_2; soluble in KOHAq and in colorless $(NH_4)_2SAq$, reprecipitated on acidulation, otherwise like SnS.

$(NH_4)_2S$ pps yellow SnS_2; soluble in excess, as thiostannate.

KOH, or *Na_2CO_3* pps white stannic acid $SnO(OH)_2$; soluble in excess of KOHAq as K stannate, or in HClAq as $SnCl_4$

NH_4OH, or *$(NH_4)_2CO_3$*, same pp; insoluble in excess.

Boiling after dilution, and especially on adding a neutral salt of an alkali as Na_2SO_4, pps metastannic acid $Sn_5O_5(OH)_{10}$; insoluble in acids; soluble in KOHAq. The same pp forms in dilute solutions on standing.

$HgCl_2$ gives no pp.

Zinc pps metallic Sn; this dissolves in warm HClAq to form a *stannous* salt, $Sn''Cl_2$, which gives a pp with $HgCl_2$, etc.

Copper reduces to $SnCl_2$, but not to metal.

Conc. HNO_3 converts metallic tin, the sulphides, and other pps, into $SnO(OH)_2$ or into metastannic acid, leaving SnO_2 on drying and igniting.

241 STANNITES AND STANNATES (derived from H_2SnO_2 and H_2SnO_3) are formed when stannous and stannic hydroxides are dissolved in KOHAq or NaOHAq: on neutralizing these solutions the hydroxides are reprecipitated, redissolving if an excess of HClAq is added, to form $SnCl_2$ or $SnCl_4$, which react as above. The stannites are strong reducing agents, *e. g.*, $K_2Sn''O_2Aq$ takes up O to form $K_2Sn^{IV}O_3Aq$ and reduces $Bi_2O_3H_2O$ to Bi_2O_2, Ag_2O to Ag, etc., and on boiling a solution part of the Sn of the stannite itself is reduced to metal.

242 THIOSTANNITES, corresponding to stannites, are formed when SnS dissolves in K_2SAq or Na_2SAq: THIOSTANNATES when SnS_2 dissolves in any alkaline sulphide solution, or SnS in a solution of one of the yellow polysulphides or of a normal sulphide mixed with S. Those of heavy metals are insoluble.

$$SnS + K_2SAq = K_2SnS_2Aq \quad (\text{or } K_2S.SnS)$$

$$SnS + K_2SAq + S = K_2SnS_3Aq \quad (\text{or } K_2S.SnS_2)$$

$$SnS + (NH_4)_2S_2Aq = (NH_4)_2SnS_3Aq \quad (\text{or } (NH_4)_2S.SnS_2)$$

Thiostannites and thiostannates are decomposed by acidulation giving precipitates of brown SnS and yellow SnS_2 respectively.

Solutions of the sulphides in KOHAq contain mixtures of stannites or stannates with the corresponding thio-salts.

243 The sulphides of As, Sb, and Sn, if dissolved in solutions of alkaline hydroxides (NaOH) or in normal colorless sulphides (Na_2S) are reprecipitated on acidulation in the same form; but if previously mixed with S, or if dissolved with the aid of yellow alkaline sulphides (containing polysulphide, *e. g.*, Na_2S_5), they are always reprecipitated by acids as the higher sulphides, *e. g.*, SnS is thus converted into SnS_2.

Even colorless alkaline sulphide solutions always contain some polysulphide, being slowly decomposed by light and becoming yellow, hence on acidulating them some free S is always deposited, white and finely divided. The sulphide used in the laboratory should only be faintly yellow, or the S thus precipitated may mask the metallic sulphides.

The solutions of the sulphides (*e. g.*, of As) in normal sulphide solutions contain thio-arsenite or thio-arsenate as the lower or higher sulphide of As was originally dissolved: the polysulphide or admixed S always yields thio-arsenate.

The solutions of the sulphides in KOHAq, or of the hydroxides or oxides in alkaline sulphides, consist of mixtures of oxy- and of thioarsenates, etc., or of still more complex salts as oxy-thio-arsenates containing O and dyad S in the same molecule, *e. g.*, Na_3AsSO_3.

244 When As, Sb, and Sn, are found in a solution of acid reaction they are present either as metallic radicals, combined with a strong acid radical (*e. g.*, —Cl), or in the case of As as free acid ($As^{III}_2O_3$ or $H_3As^VO_4$); in alkaline solutions they exist in the acid radicals combined with some alkali-metal, *e. g.*, an arsenite or arsenate, or the corresponding Sb or Sn compound: if on acidulating the alkaline solution a pp of sulphide (colored) forms, a *thio*-arsenite, etc., is present, pp being usually accompanied by evolution of H_2S: the thio-salts also pp black PbS when treated with $Pb(C_2H_3O_2)_2$ or K_2PbO_2.

To distinguish the different degrees of oxidation in the oxy-salts KI or I (with starch paste) may be used after slightly acidulating with HClAq: I is set free from HI by Sb^V while free I is reduced to HI by Sn'' or As^{III}.

Rarer Elements of the Arsenic Group.

245 GOLD: Au''' Au' (and Au'').

BLOWPIPE REACTIONS: when heated on charcoal all compounds are reduced even in O.F. to yellow fusible metal, very malleable if pure, but color and malleability are much affected by presence of Pb, Sn, etc. If combined with non-metals or metals which are readily oxidized it may easily be purified by fusing in O.F. in contact with a little borax, or by alloying with several times its weight of lead and cupelling (204 *note*) on boneash.

AURIC SALTS: Au'''.

REACTIONS IN SOLUTION: use $HAuCl_4Aq$ ($HCl.AuCl_3$).

N. B. This compound, chlorauric acid, is formed when gold or any of its compounds is dissolved in aqua regia, evaporated almost to dryness with an excess of HCl, and the residue dissolved in water. The solution is deep yellow. The H is replacable by metals to form chloraurates, *e. g.*, $KAuCl_4$.

H_2S pps brown or black AuS (Au_2S_2) insoluble in single acids, soluble in yellow $(NH_4)_2S_xAq$ or Na_2S_xAq (as thio-salts, *e. g.*, Na_3AuS_3), in KCNAq and in aqua regia. From hot solutions the pp contains metallic Au.

$(NH_4)_2S$ or $Na_2S_2O_3$ pps sulphide, soluble in large excess.

Zinc and nearly all other metals pp metallic gold.

$FeSO_4$, $SnCl_2$, KNO_2, SO_2, As_2O_3, and most other reducing agents, pp finely divided metallic gold, varying in color—often yellow or brown by reflected, green or purple by transmitted light, or as a yellow mirror on the containing vessel: $H_2C_2O_4$ or H_2S gives the same pp from a hot solution. The metal is readily dissolved by aqua regia, and by ClAq or BrAq, more readily in presence of NaCl or KBr (forming $AuCl_3$ or $KAuBr_4$ etc.), and by KCNAq in presence of air or oxidizing agents.

$SnCl_2$, after adding $FeCl_3$, gives a pp of "Purple of Cassius."

If filter paper is moistened with any gold solution, dried, and burned, the ash has a purple color: treating paper with HNO_3Aq facilitates burning.

The metal (in presence of air or oxidizing agents) and nearly all compounds dissolve in KCNAq to form POTASSIUM GOLD CYANIDES ($KAu'Cy_2$ and $KAu'''Cy_4$) which are soluble in water and not precipitable by the ordinary reagents, they may be decomposed by evaporating to dryness with H_2SO_4 or aqua regia, heating the residue and redissolving in BrAq or dilute aqua regia.

246 PLATINUM: Pt^{iv} and Pt''.

BLOWPIPE TESTS: when heated on charcoal all compounds are reduced to infusible gray metal. Addition of As or Pb makes it readily fusible: cupelled with Pb it leaves an infusible gray mass.

PLATINIC SALTS: Pt^{iv}.

REACTIONS IN SOLUTION: use H_2PtCl_6 (chloroplatinic acid).

N. B. Chloroplatinic acid is formed when platinum or any of its compounds is dissolved in aqua regia, evaporated with HCl, and redissolved in water. The solution is reddish brown, like $FeCl_3Aq$.

NH_4Cl pps yellow crystalline $(NH_4)_2PtCl_6$ (ammonium chloroplatinate), but not from very dilute solutions: pp is somewhat soluble in water, insoluble in alcohol or ether.

H_2S pps dark brown PtS_2, an excess forming light brown H_2PtS_3. Pp resembles AuS in solubility, with $(NH_4)_2S_x$ Aq it dissolves as a soluble thio-platinate, $(NH_4)_2PtS_3$.

Reducing agents affect Pt salts less readily than those of Au: *e. g.*, *SO_2* and *$H_2C_2O_4$* give no pps even from hot solutions: *$SnCl_2$* gives no pp but causes a darkening in color, owing to formation of a Pt'' compound: *$FeSO_4$* pps Pt on long boiling: metallic *zinc* pps Pt. The metal thus ppd is slowly dissolved by aqua regia, ClAq, or BrAq.

247 TELLURIUM: $Te^{\text{ii iv or vi}}$, like S, see 112.

BLOWPIPE TESTS: heated in closed tube Te volatilizes and forms a sublimate of black Te with some white TeO_2: some of its compounds give same reaction. On C in O.F. Te and tellurides give a white sublimate resembling that of Sb, and flame is colored greenish. Heated with Na_2CO_3 and C in a closed tube Na_2Te forms, on cooling and adding water this dissolves to a purplish color: solution blackens silver like Na_2S.

REACTIONS IN THE WET WAY: Te and most non-oxidized compounds, warmed with conc. H_2SO_4, give a carmine liquid, $STeO_3$, easily decomposed by stronger heating or on standing.

Sodium amalgam, stirred with a wetted Te compound, gives violet Na_2TeAq.

Hot conc. HNO_3 converts Te and most compounds to H_2TeO_3 (tellurous acid), somewhat soluble in acids, soluble in KOHAq as K_2TeO_3 (tellurite). On acidulating this with *HCl* and adding H_2S black TeS_2 is ppd, soluble in KOHAq or $(NH_4)_2S_xAq$, insoluble in KCNAq.

Reducing agents, $SnCl_2$, SO_2, $Zn + HClAq$, etc., pp black Te, insoluble in KCNAq.

248 SELENIUM: $Se^{II\ IV\ or\ VI}$, like S, see 112.

BLOWPIPE TESTS: in closed tube Se itself sublimes as red or black Se, with characteristic fetid odor. Heated on charcoal with Na_2CO_3 in R.F. componnds leave Na_2Se, solution of which blackens silver like Na_2S: with HCl gives off H_2Se resembling H_2S. Se burns with blue flame like S.

REACTIONS IN THE WET WAY: *conc.* HNO_3 converts Se and most compounds into SeO_2, soluble in water, acids or alkalis. H_2S, after acidulating with HCl, pps yellow SeS_2, closely resembling As_2S_3 in solubilities, on heating becomes orange (Se + S), soluble in KCNAq as KCNSe whence Se is reppd on acidulation.

Reducing agents, $HCl + Zn$, $SnCl_2$, SO_2, pp red Se, soluble in KCNAq; $HCl + Cu$ slowly pps red Se, but $FeSO_4$ gives no pp.

SELENITES and SELENATES of the alkali metals are soluble and resemble sulphites and sulphates, but are ppd by HCl + H_2S.

249 MOLYBDENUM: $Mo^{IV\ VI\ etc.}$ Chiefly met with as MoS_2, MoO_3 and in molybdates.

BLOWPIPE TESTS: borax bead is yellow to colorless in O.F., dark brown in R.F. $NaPO_3$ bead is green in either flame, after O.F. it becomes lighter on cooling. On C. in O.F. a white sublimate of MoO_3 forms; R.F., applied to sublimate, reduces it to a *blue* oxide and finally volatilizes it leaving a coppery stain (MoO). Heated with a drop of conc. H_2SO_4 on platinum foil, evaporated almost to dryness, cooled, and breathed upon, a blue compound is formed. Oxides color O.F. green, very like Ba.

REACTIONS IN THE WET WAY: *conc.* HNO_3 yields white H_2MoO_4 from most compounds, soluble in NH_4OHAq (as ammonium molybdate), or in an excess of acid. With the HNO_3Aq solution H_2S gives a blue color and then a black pp of MoS_3 (soluble in $(NH_4)_2SAq$), $SnCl_2$ gives a blue color, $Na_2HPO_4 + NH_4Cl$ gives a yellow pp soluble in NH_4OHAq. From solutions of ammonium molybdates acidulation pps H_2MoO_4, resembling H_2WO_4 but more readily soluble in an excess of acid.

250 GERMANIUM: Ge'' or iv, Ge resembles Sn in its reactions and the properties of its compounds; GeS_2 is white.

IRIDIUM: $Ir^{III \text{ or } IV}$. Ir is infusible and almost insoluble in aqua regia. Solutions usually contain $IrCl_4$ or $IrCl_3$, its reactions resembling those of Pt: H_2S pps Ir_2S_3; $FeSO_4$ and NH_4Cl give no pps.

251 Separation of As, Sb, and Sn.

From the Copper and Silver groups, similarly ppd by H_2S, these metals are separated by their sulphides being soluble in KOHAq or in alkaline sulphide solution, whence they are reprecipitated by acidulation.

From the mixed sulphides of As, Sb, and Sn, that of As can be separated by its solubility in NH_4HCO_3Aq or $NaHSO_3Aq$, or by its insolubility in HClAq.

Sb and Sn may be distinguished by the action of a zinc-platinum couple on their chlorides; Sb being ppd on the platinum, Sn on the zinc: the latter can be dissolved in HClAq as $Sn''Cl_2$ in which condition it pps $HgCl_2Aq$ or $HAuCl_4$. Or the solution is treated with an excess of oxalic acid and H_2S, Sb is ppd but not Sn.

From a solution of the chlorides As and Sb can also be separated by $Na_2S_2O_3$, which pps them but not Sn as sulphides which can be separated as above.

As can also be detected by the Marsh apparatus, but in this case the mixed sulphides are dissolved by $HClAq + KClO_3$: or by conversion into arsenic acid.

The gases from the Marsh apparatus may be passed into $AgNO_3Aq$; AsH_3 pps Ag and gives a solution of H_3AsO_3, while SbH_3 pps Ag_3Sb which can be treated with tartaric acid and tested by H_2S for Sb.

Gold, in ores, etc., is rarely found in large enough proportion to affect the separation of the As group: if necessary, it, with Te and Se, may be first ppd by SO_2Aq: or the Au may be removed by boiling with oxalic acid, and Pt by concentrating and adding NH_4Cl.

METALS PRECIPITATED BY AMMONIUM SULPHIDE, BUT NOT BY HYDROGEN SULPHIDE FROM ACID SOLUTIONS.

IRON GROUPS.

252 These comprise the metals of the earths and the more positive of the heavy metals, and may be divided into two sections:—those precipitated by ammonia in the presence of ammonium chloride, and those whose hydroxides are soluble in ammonium chloride. The first includes aluminium, chromium, and the other earth metals (mostly of triad valence), iron (in ferric salts) and uranium: nearly all but the last two are precipitated by ammonium sulphide as *hydroxides*, the sulphides not being formed in presence of water. The latter group comprises dyad metals precipitated as *sulphides*.

TRIAD METALS OF THE IRON GROUP.

(With which are included metals of the rarer earths.)

Al, Cr in chromic salts, Fe in ferric salts.

253 These form oxides and chlorides of the type R_2O_3, RCl_3, and their sulphates combine with those of the alkali-metals to form alums, *e. g.*, $KAl(SO_4)_2.12aq$, crystallizing in regular octahedra. Their salts tend to decompose when heated, losing acid; the hydroxides when boiled lose water, and become difficultly soluble in acids, if ignited they become insoluble. Ammonia precipitates them all as hydroxides, $R_2O_3.xaq$, nearly insoluble in excess or in NH_4ClAq; alkaline carbonates precipitate hydroxides, or highly basic carbonates, most of the CO_2 escaping; if shaken up with $BaCO_3$ the same reaction takes place. Sodium phosphate precipitates their normal phosphates (RPO_4) insoluble in acetic acid. Boiled with an alkaline acetate they are thrown down as basic acetates, insoluble in *hot* water.

With this group fall uranium and the rare earth-metals, the reactions of most of which bear a general resemblance to those of Al. Some of these (of which Ti is the commonest), are tetrads.

With ammonium sulphide their behavior is generally abnormal, Al, Cr and the rarer earths are precipitated as ***hydroxides*** with escape of H_2S, Fe''' forms $Fe''S$ and free S, U forms an oxysulphide.

ALUMINIUM: Al'''.

254 BLOWPIPE TESTS: compounds are generally white or colorless; heated on charcoal they leave white infusible residues, glowing while hot; if these are cooled, moistened with a cobalt solution, and again strongly heated they form sky blue $CoAl_2O_4$, cobalt aluminate, or Thenard's blue.

255 REACTIONS IN SOLUTION: use $Al_2(SO_4)_3Aq$ or ammonia alum $NH_4Al(SO_4)_2Aq$.

NH_4OH pps whitish, gelatinous $Al(OH)_3$, soluble in acids or KOHAq, almost insoluble in NH_4OHAq and in NH_4ClAq; best seen after heating and allowing to stand a few minutes. If any organic coloring matter is present the pp usually carries it down as a "lake."

KOH pps whitish $Al(OH)_3$ readily soluble in excess as $KAlO_2$ (K aluminate, see 138) re-ppd by NH_4Cl or by careful neutralization (as by HCl or CO_2) but not ppd by boiling.

$(NH_4)_2S$ pps $Al(OH)_3$, H_2S escaping (140).

H_2S gives no pp.

Nearly all the Al pps are dissolved by KOHAq to form aluminates.

ALUMINATES are derived from the acid $HAlO_2$ or $Al_2O_3H_2O$, those of K and Na being soluble and not decomposed by boiling (compare zincates 276), but decomposed by NH_4Cl or by acids (138).

CHROMIUM: $Cr'''^{\,\mathrm{VI\ and}\,''}$.

256 BLOWPIPE TESTS: most compounds are strongly colored: those of Cr''' usually violet or green, of Cr^{VI} yellow to red. Heated alone on charcoal many compounds yield green infusible Cr_2O_3. In borax all give green beads in O.F. and R.F., somewhat reddish while hot in O.F.; $NaPO_3$ gives similar colors. Fused on platinum with four or five volumes of dry Na_2CO_3 and one of $KClO_3$ all compounds are oxidized to yellow Na_2CrO_4, which is soluble in water.* An alkaline flux with any oxidizing agent, even air, gives a similar result.

CHROMIC SALTS: Cr'''

257 REACTIONS IN SOLUTION: use $CrCl_3Aq$ or $KCr(SO_4)_2Aq$ (chrome alum).

NH_4OH pps greenish $Cr(OH)_3$. This is slightly soluble (pink) in an excess of ammonia (if strong and cold) but is re-ppd on boiling.

KOH pps greenish $Cr(OH)_3$ soluble in excess as $KCrO_2$ (green K chromite): re-ppd by long boiling, by NH_4Cl, or on neutralizing; soluble in acids.

$(NH_4)_2S$ pps $Cr(OH)_3$, H_2S escaping; insoluble in excess.

H_2S gives no pp.

258 CHROMITES, derived from the anhydride Cr_2O_3 occur in the green solutions obtained by treating the $Cr(OH)_3$ with excess of KOH or NaOH; ppd by boiling or neutralization; *HCl* in excess yields $CrCl_3$ Aq.

CHROMOUS SALTS, containing Cr'' are rarely met with and easily oxidize to Cr'''. $CrCl_2$ is white.

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*The mineral *chromite* (ferrous chromite $FeCrO_2$) is almost insoluble in acids and reacts very slowly with fluxes; it is readily converted into soluble yellow $Na_2 CrO_4$ if fused with sodium peroxide, Na_2O_2. Fused with alkalis the tendency is for all compounds to form chromates, heated with acids, to form chromic salts.

259 CHROMATES AND DICHROMATES: Cr^{VI}: use $K_2Cr_2O_7Aq$. These are derived from chromic acid (H_2CrO_4) and dichromic acid ($H_2Cr_2O_7$) and from the anhydride CrO_3. The alkali-metal salts are readily soluble: a solution of acid reaction is orange or reddish, and contains dichromate; on neutralizing with an alkali it becomes a pale yellow and contains a chromate. They are strong oxidizing agents, and easily reduced in presence of acid to green Cr''' salts.

With solutions not far from neutral:

$Pb(C_2H_3O_2)_2$ gives yellow $PbCrO_4$ (chrome yellow), soluble in KOHAq, insoluble in acetic acid, or highly dilute HNO_3Aq.

$BaCl_2$ pps yellow $BaCrO_4$, soluble in HClAq, but not in acetic acid.

$AgNO_3$ pps reddish Ag_2CrO_4 or $Ag_2Cr_2O_7$, soluble in HNO_3Aq or NH_4OHAq.

H_2S, after acidulating strongly with *HCl* pps S, forming green $CrCl_3Aq$ (see 140). *Conc. HClAq* alone slowly reduces chromates to $CrCl_3$, evolving Cl, more readily in presence of reducing agents, *e. g.*, alcohol. $Fe''SO_4$ is oxidized to Fe''' salt.

$(NH_4)_2S$ pps greenish $Cr(OH)_3$, mixed with S.

With solid chromates, or strong solutions:

Conc. H_2SO_4 gives red crystals (CrO_3) soluble in water: *conc.* H_2SO_4 + *HClAq* (or a chloride) gives red fumes of volatile CrO_2Cl_2 (chloro-chromic anhydride).

IRON: $Fe^{II \text{ and } III}$.

260 BLOWPIPE TESTS: Heated on charcoal, all iron compounds leave dark residues, magnetic on cooling. Heated with Na_2CO_3 or KCN on charcoal in R.F., metallic iron is reduced as a magnetic powder. Borax bead, in O.F., is yellow to red while hot, yellowish cold; in R.F., greenish, the differing colors being due to Fe^{III} and Fe^{II} compounds.

The $NaPO_3$ bead is yellow to reddish hot, lighter cold, passing through a greenish shade while cooling.

261 FERRIC SALTS: Fe^{III}.

Reactions in Solution: use $FeCl_3Aq$. Compare Fe^{II} (267). Ferric salts and solutions are generally reddish-brown or yellow, the colors varying with temperature.

They are reduced to the ferrous state (Fe^{II}) by most reducing agents—$SnCl_2$, SO_2 (heated), $Zn + HCl$, $Al + HCl$, and H_2S are often used. See 267.

NH_4OH pps red-brown $Fe(OH)_3$ or $Fe_2O_3.x aq$, insoluble in excess or in NH_4ClAq, soluble in $HClAq$ and other strong acids. With H_2S or $(NH_4)_2S$ this pp yields black $2FeS + S$. If heated, $Fe(OH)_3$ leaves Fe_2O_3, very difficultly soluble in acids but dissolved by $HClAq$ in presence of $SnCl_2$.

KOH pps $Fe(OH)_3$, insoluble in excess; pp always retains alkali.

H_2S pps finely divided S, forming a ferrous salt and removing yellow color (140).

$(NH_4)_2S$ pps black *ferrous* sulphide mixed with S ($2FeS + S$), insoluble in excess, but dissolved by $HClAq$, leaving free S.

K_4FeCy_6 gives a blue pp, $Fe_4(Fe^{II}Cy_6)_3$ (prussian blue), slightly soluble in excess, decomposed by $KOHAq$, NH_4OHAq, or conc. acids: solution should be acidulated with HCl or $HC_2H_3O_2$ before testing.

K_3FeCy_6 gives a green or brown color, but *no blue pp* on acidulating: addition of a reducing agent (a drop of $SnCl_2Aq$) gives color of Prussian blue.

$KCNS$ or *NH_4CNS* after acidulating gives red color, due to soluble $Fe(CNS)_3$: $HgCl_2$ removes color, forming $Hg(CNS)_2$.

Tannic acid, and solutions of galls, give bluish-black pps or colorations.

Na_2HPO_4 pps yellowish white $FePO_4$, almost insoluble in acetic acid, soluble in $HClAq$. Reaction sets some HCl free, and precipitation is complete only when neutralized, or on adding some alkaline acetate ($NH_4C_2H_3O_2$).

If a solution containing Fe^{III} and H_3PO_4, or a phosphate dissolved in acid, is neutralized by NH_4OH, $FePO_4$ is thrown down with the $Fe(OH)_3$, and if sufficient iron is present all the PO_4 will be carried down with it, in preference to dyad metals (262).

$NH_4(C_2H_3O_2)$ or *$NaC_2H_3O_2$* (alkaline acetates), added to a nearly neutral solution of $FeCl_3$ gives a red solution of $Fe(C_2H_3O_2)_3$, and when boiled pps brown basic ferric acetate, insoluble in hot water, some $HC_2H_3O_2$ being set free (142). In presence of phosphoric acid or a dissolved phosphate the basic acetate carries down all the PO_4 as $FePO_4$, provided enough iron is present.*

FERRITES are derived from the acid H_2FeO_2 and anhydride Fe_2O_3, and are insoluble in water: precipitated $Fe(OH)_3$ tends to carry down dyad and alkali metals with it, apparently combined as ferrites.

FERRATES, derived from H_2FeO_4, contain Fe^{VI}: they are unstable; purplish K_2FeO_4 is obtained when Fe compounds are fused with $K_2CO_3 + KClO_3$.

262 With alkaline phosphates and acetates the behavior of Cr and Al is like that of Fe^{III}; $AlPO_4$ is somewhat more soluble in acetic acid than the others. The Cr pps are greenish, those of Al whitish, like the hydroxides: towards KOH and $(NH_4)_2S$ they act much like the hydroxides, and can be separated in the same way from one another. The precipitation with basic acetate, or with $BaCO_3$, separates these three metal from nearly all others.

The precipitated hydroxides, phosphates, and basic acetates, especially the latter, are gelatinous or slimy, and should be filtered hot after boiling a short time.

The presence of sugars, and of certain organic acids (citric and tartaric), prevents the precipitation of these metals by ammonia, and retards the action of other reagents. In analysis such organic matter is removed by evaporating with HNO_3 and igniting.

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* This also holds good for Al and Cr.

Phosphoric acid combines with either when precipitated by ammonia, in preference to other metals.

263 URANIUM: $U^{VI \text{ and } IV}$. Usually met with as oxide or in salts of uranyl $(U^{VI}O_2)^{II}$.

Blowpipe Tests: use UO_3. Borax bead is like Fe: yellow to red hot in O.F., lighter cold. $NaPO_3$ bead is yellowish hot in O.F., yellow green cold, and in R.F. green like Cr.

Reactions in Solution: use $(UO_2)(NO_3)_2$ or $UO_2(C_2H_3O_2)_2$—uranyl nitrate or acetate. The ordinary salts are compounds of the radical uranyl $(UO_2)^{II}$; the crystals and solutions are greenish yellow.

$(NH_4)OH$ and *KOH* give pps of acid alkali-metal uranate $K_2O.xUO_3$, etc., soluble in excess of $(NH_4)_2CO_3$ and in acids.

$(NH_4)_2S$ pps brown UO_2S (with some $(NH_4)_2S$), insoluble in excess, on heating yields black UO_2+S; the pp of UO_2S is soluble in $(NH_4)_2CO_3Aq$.

Na_2CO_3 or *$(NH_4)_2CO_3$* pps an alkali-uranyl carbonate, soluble in excess, on neutralization pps an acid uranate.

K_4FeCy_6 gives a brown pp, insoluble in acetic acid.

Na_2HPO_4 pps greenish white UO_2HPO_4xaq, insoluble in acetic acid or $(NH_4)C_2H_3O_2Aq$; all soluble phosphates, and arsenates, give similar pps in acetic acid solutions of U.

264 TITANIUM: $Ti^{IV \text{ and } III}$. Usually met as TiO_2 or in insoluble titanates.

Blowpipe Test: Oxide is yellowish, infusible, fused with Na_2CO_3 effervesces like SiO_2. The $NaPO_3$ bead in R.F. is yellowish hot, lavender or violet cold: in presence of Fe this becomes blood red: in O.F. the bead is nearly colorless.

Reactions in Solution: use a solution containing $Ti(SO_4)_2$. This may be prepared by prolonged fusion of the oxide with $HKSO_4$, cooling and extracting with cold water, or by fusion with Na_2CO_3 and dissolving in H_2SO_4Aq. $TiCl_4Aq$ is slowly formed by treatment of the oxide with strong HClAq. These solutions are very unstable: TiO_2 acts as a very weak base or as an acid, having analogies to SnO_2 and SiO_2.

Metallic Zinc reduces Ti^{IV} solutions to Ti^{III} compounds, the solution becoming violet.

Boiling, especially after dilution, gradually pps white $Ti(OH)_4$.

NH_4OH pps $Ti(OH)_4$, insoluble in excess, soluble in acids.

H_2O_2 gives a yellow to amber color with solutions of $Ti(SO_4)_2$.

265 The rare earth-metals GLUCINUM (or Beryllium Gl''), ZIRCONIUM (Zr^{IV}), THORIUM (Th^{IV}), CERIUM (Ce''' $^{\text{and IV}}$), YTTRIUM (Y'''), LANTHANUM (La'''), DIDYMIUM (Di''' or Neodymium, Nd, and Praseodymium, Prd), and a few others are precipitated by NH_4OH as $Gl(OH)_2$, $Zr(OH)_4$, $Th(OH)_4$, $Ce(OH)_3$, $Y(OH)_3$, $La(OH)_3$, and $Di(OH)_3$, etc.; KOH and $(NH_4)_2S$ give the same pps.

Gl salts have a sweetish taste and resemble those of Al; $Gl(OH)_2$ is soluble in KOHAq like $Al(OH)_3$ and unlike the others. All the others are ppd as oxalates on addition of excess of $(NH_4)_2C_2O_4$ or $H_2C_2O_4$; on ignition these leave the oxides. Conc. K_2SO_4Aq pps the same metals as double sulphates. When strongly heated the oxides are highly incandescent. Ce_2O_3 on ignition becomes orange CeO_2, the Ce''' salts are colorless with sweetish astringent taste, Ce^{IV} salts are orange: concentrated solutions of Di salts are faintly violet. With $NaPO_3$ in O.F. Ce gives yellow to red beads while hot, colorless cold, Di gives light amethyst color: both are colorless in O.F. The others give no readily observed blowpipe tests.

$Na_2S_2O_3$ pps Ti, Zr and Th as hydroxides, separating them from the others, and from iron group generally.

THALLIUM (Tl''') and INDIUM (In''') are ppd by ammonia as (TlO)OH and $In(OH)_3$, detected by green and blue spectroscopic lines: GALLIUM (Ga''') is thrown down as $Ga(OH)_3$ but redissolved by excess of ammonia; $(NH_4)_2S$ pps it as Ga_2S_3, and converts the Tl and In pps into Tl_2S_3 and In_2S_3.

TANTALUM (Ta^{V}) and COLUMBIUM (Cb^{V} or Nb) are ppd as Ta_2O_5 and Cb_2O_5 from solutions of the alkaline tantalates and columbates (derived from the anhydrides) on acidulation with HCl, but dissolve (Cb with some difficulty) in an excess of HClAq. From the acid solutions *NH_4OH* pps the oxides with the iron group. *Zinc* gives blue and finally brown reduction products with Cb in HClAq solution. With $NaPO_3$ Cb gives a blue to brown bead in R.F., Ta colorless beads.

DYAD METALS OF THE IRON GROUP.

Fe″ in ferrous salts, Mn″, Ni, Co, Zn.

266 These are all precipitated by $(NH_4)_2S$ as sulphides; if exposed to air the precipitates tend to oxidize to sulphates.

H_2S does not precipitate them in presence of free strong acid, but precipitates them partially from neutral solutions (*i. e.*, until the acid set free prevents further action), completely from ammoniacal solutions, and (except Mn) completely from the acetates.

NH_4OH only precipitates them partially, as the hydroxides are all soluble either in excess of NH_4OHAq or in solutions of ammonium salts: and if much ammonium salt or free acid is originally present it gives no precipitates at all. This is due to the formation of double ammonium chlorides, etc. (*e. g.*, MCl_2xNH_4Cl where $x = 1$ to 3), these double ammonium salts being very stable and not affected by NH_4OH, though decomposed by boiling KOHAq. Compare Mg. KOH precipitates the hydroxides, that of Zn being soluble in excess, and all in KCNAq. The hydroxides, and ammoniacal solutions, are converted into sulphides by H_2S or alkaline sulphides. Na_2HPO_4 precipitates them as phosphates, and alkaline carbonates as carbonates, both having solubilities similar to those of the respective hydroxides and being similarly decomposed by H_2S or $(NH_4)_2S$.

$BaCO_3$ does not affect the nitrates, chlorides or acetates; the acetates are not affected by boiling.

Like Cu″, Cd and Mg they form double sulphates with K or (NH_4), *e. g.*, $K_2Ni(SO_4)_2.6aq$.

267 FERROUS SALTS: Fe″. For dry tests see 260.

Reactions in Solution: use $FeSO_4Aq$, compare 261. Crystallized salts and solutions are pale green to colorless.

They are readily oxidized to ferric salts by BrAq or ClAq, or on boiling with a little conc. HNO_3, slowly by simple exposure to air: solutions usually contain traces of ferric salt.

NH_4OH pps, incompletely, dull green $Fe(OH)_2$ [pure $Fe(OH)_2$ is white]; by absorption of O this darkens, finally becoming red-brown Fe_2O_3xaq; original pp is somewhat soluble in NH_4ClAq, but solution absorbs O and deposits brown $Fe(OH)_3$.*

KOH pps dull green $Fe(OH)_2$, insoluble in excess, soluble in acids.*

$(NH_4)_2S$ pps black FeS, insoluble in excess or in NH_4ClAq, completely soluble in dilute HClAq. FeS oxidizes easily to $FeSO_4$.

K_4FeCy_6 pps light blue $K_2Fe''_3(Fe''Cy_6)_2$ insoluble in dilute acids; oxidizes readily to dark Prussian blue $Fe'''_4(Fe''Cy_6)_3$.

K_3FeCy_6 pps dark Turnbull's blue, $Fe''_3(Fe'''Cy_6)_2$ resembling Prussian blue.

N. B. These blue pps are decomposed by alkalis, solutions should be made slightly acid before testing.

$KCNS$ or NH_4CNS usually gives a slight red color, due to admixed ferric salts; no reactions with pure ferrous salts.

MANGANESE: $Mn^{II\ III\ IV\ VI\ VII}$.

268 BLOWPIPE TESTS: Fused on platinum foil with Na_2CO_3 and a little $KClO_3$ all compounds yield a green or bluish-green manganate, Na_2MnO_4. [This dissolves in water, forming purple permanganate, $NaMnO_4$, and giving a brown pp of MnO_2—if solution remains green adding a few drops HClAq hastens change.] The borax bead is violet in O.F. while hot, lighter (amethyst) on cooling, colorless in R.F., forming manganic and manganous compounds respectively; $NaPO_3$ is similarly colored.

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*From mixtures of Fe'' and Fe''' salts in certain proportions alkalis give a black pp of Fe_3O_4.

269 MANGANOUS SALTS: Mn^{II}.

REACTIONS IN SOLUTION: use $MnCl_2Aq$. Solutions and crystallized salts are generally pink or colorless; some show a tendency to become brown, forming manganic compounds.

NH_4OH pps, incompletely, whitish $Mn(OH)_2$, insoluble in excess, but soluble in NH_4ClAq or in acids; readily oxidized, on exposure, to dark brown Mn_2O_3xaq, or Mn_3O_4 insoluble in NH_4ClAq. The NH_4Cl solution, containing ammonium manganous chloride, is oxidized by air, brown $Mn(OH)_3$ falling out: *BrAq* pps MnO_2xaq from it.

KOH pps whitish Mn $(OH)_2$, insoluble in excess: with BrAq black MnO_2xaq forms.

$(NH_4)_2S$ pps MnS, pink or greenish yellow, insoluble in excess or in NH_4ClAq; soluble in dilute acids (even *acetic*), this distinguishes it from rest of group.

270 HIGHER OXIDES OF MANGANESE.

MANGANIC COMPOUNDS: Mn''' and Mn^{IV}. The higher oxides MnO_2, Mn_2O_3, Mn_3O_4), heated with HClAq, evolve Cl and finally yield $MnCl_2$, but before expulsion of all Cl the solutions are brown, and contain $MnCl_3$ or $MnCl_4$, from which NH_4OH or KOH pps brown $Mn(OH)_3$.

MANGANATES (*e. g.*, K_2MnO_4) are derived from the anhydride MnO_3, alkaline manganates are green and soluble in water to green solutions, which decompose, giving pps of MnO_2 and forming red or purple solutions containing permanganates.

PERMANGANATES are derived from the acid $HMnO_4$ and anhydride Mn_2O_7, the alkali-metal salts are soluble, giving purple solutions: use $KMnO_4Aq$. With excess of KOH these become green; reducing agents decolorize them, giving pps of MnO_2 etc., in neutral solutions which undergo changes of color, or forming colorless Mn'' salts in presence of free acid.

NICKEL: Ni''.

271 Blowpipe Tests: heated on charcoal with Na_2CO_3 or KCN in R.F. all compounds leave magnetic particles, which appear silvery white when the residue is rubbed in a mortar. The borax bead in O.F. is violet while hot, suddenly changing to brown cold; in R.F. it becomes clouded, and is colorless after very long treatment: $NaPO_3$ bead is yellowish to red while hot, lighter cold, resembling that of Fe. On heating alone most salts change from green to nearly black.

272 Reactions in Solution: use $NiSO_4Aq$, or $NiCl_2Aq$. Crystallized salts and solutions are usually green: on evaporating to dryness the green residues lose water, usually becoming yellow.

NH_4OH gives a slight greenish pp of $Ni(OH)_2$, readily soluble in excess or in NH_4ClAq, hence no pp forms from solutions originally acid; with excess of NH_4OH solution is usually blue.

KOH pps apple green $Ni(OH)_2$, insoluble in excess.

Na_2CO_3 or *$(NH_4)_2CO_3$* gives green pp, soluble in ammonium salts.

$(NH_4)_2S$ pps black NiS, somewhat soluble in excess (liquid becoming dark brown, especially if free ammonia and polysulphide are present) and re-ppd by long boiling or by acetic acid: pp is nearly insoluble in dilute HClAq, soluble in warm HNO_3Aq or aqua regia, and in KCNAq.

H_2S gives no pp from solutions containing free HCl, but from alkaline solutions, or acetates, pps NiS.

COBALT: Co'' and'''.

273 Blowpipe Tests: heated on charcoal in R.F. with Na_2CO_3 or KCN compounds leave a magnetic residue. Borax bead is a strong blue in either flame, $NaPO_3$ bead a similar color.

274 REACTIONS IN SOLUTION: use $CoCl_2$ or $Co(NO_3)_2$.

Solutions are usually rose-colored, on evaporation to near dryness with HClAq, they become blue and leave pink residues, which turn blue on expelling water, and are finally decomposed by ignition, leaving black oxide.

NH_4OH gives a slight blue pp of basic salt, almost completely soluble in excess (to brownish liquid) or in NH_4ClAq.

KOH pps a blue basic salt or rose-colored $Co(OH)_2$, insoluble in excess, soluble in ammonium salts; on exposure oxidizes to olive green or brown $Co(OH)_3$, insoluble in NH_4ClAq.

Na_2CO_3 or *$(NH_4)_2CO_3$* gives a peach-colored pp, blue on boiling, soluble in ammonium salts.

$(NH_4)_2S$ pps black CoS, insoluble in dilute HClAq, soluble in HNO_3Aq, KCNAq etc., closely resembling NiS but insoluble in excess of $(NH_4)_2SAq$.

KNO_2, added in excess to a solution containing free acetic acid, pps yellow crystalline $2K_3Co'''(NO_2)_6.3aq$, potassium cobaltic nitrite.

ZINC: Zn''.

275 BLOWPIPE TESTS: use both $ZnSO_4$ and ZnS.

N. B. Compounds are usually white, the pure sulphide included. Heated on charcoal most compounds leave a whitish residue, and in R.F. (especially if mixed with KCN) all give a sublimate of ZnO, very near assay. Both sublimate and residue are white when cold, yellow while hot, non-volatile in R.F., and on strong heating glow with a peculiar greenish light. If either is cooled, moistened with a drop of *dilute* $Co(NO_3)_2Aq$ and again strongly heated in O.F., cobaltous zincate ($CoO.xZnO$, Rinman's green) remains, of a characteristic light green color. Beads of metallic zinc cannot be obtained by the blowpipe, the metal is reduced from oxide by R.F., and from ZnS, etc., by fused KCN, but immediately volatilizes: the formation of the sublimate depends on this fact, as compounds of zinc are generally non-volatile.

276 Reactions in Solution: use $ZnCl_2Aq$ or $ZnSO_4Aq$.

NH_4OH pps white $Zn(OH)_2$, readily soluble in excess (as zincate), soluble in $(NH)_4ClAq$ (as double chloride, NH_4ZnCl_3, etc.): the solution in NH_4OHAq is mostly re-ppd on boiling.

KOH pps white $Zn(OH)_2$, soluble in excess (as K zincate, K_2ZnO_2); most of the zinc is re-ppd as ZnO on diluting and boiling, not by adding NH_4Cl (compare Al 254).

$(NH_4)_2S$ pps white ZnS, insoluble in excess, in alkalis or in NH_4ClAq, soluble in dilute acids except acetic.

H_2S gives no pp with solutions containing a fair proportion of free HCl, but pps ZnS from acetates and alkaline solutions, partially from neutral solutions.

KCN pps gelatinous white $ZnCy_2$, readily soluble in excess.

K_4FeCy_6 pps white slimy Zn_2FeCy_6 or $K_2Zn_3\ (FeCy_6)_2$, insoluble in acetic acid, or sufficiently dilute HClAq.

Na_2CO_3 pps white basic carbonate, insoluble in excess, somewhat soluble in NH_4OHAq and ammonium salts.

Nearly all zinc compounds (except ZnS) dissolve very readily in KCNAq, forming K_2ZnCy_4, and most precipitates (except ZnS) dissolve in an excess of KOHAq or NH_4OHAq, forming zincates. The double cyanide is stable, not affected by boiling, on neutralizing the zinc is ppd, usually as $ZnCy_2$ soluble in dilute HClAq on warming.

Zincates, derived from the anhydride ZnO, exist in the solutions containing excess of alkaline hydroxide: they are unstable and only form in presence of an excess of alkali (*e. g.*, $K_2ZnO_2 + 4KOH$), on diluting and boiling ZnO is ppd, but not completely if a large proportion of KOH is present; NH_4Cl does not pp zincates like aluminates, unless boiled, as $Zn\ (OH)_2$ is soluble in NH_4OHAq.

Separation of Metals of the Iron Groups.

277 The metals of the iron group may, after removal of silver, copper, and arsenic groups by H_2S, be precipitated all at once by $(NH_4)_2S$—preferably after neutralizing with ammonia—or by making strongly alkaline and passing gaseous H_2S. Or they may be divided into two sections by first precipitating with NH_4OH and NH_4Cl to remove Al, Cr and Fe''', etc., and adding $(NH_4)_2S$ after filtering. The latter method gives an imperfect separation, and requires certain precautions, but has some advantages: reprecipitation is often advisable (see 514).

If all are thrown down together the precipitate may be dissolved in hot dilute HNO_3Aq, aqua regia, or $HClAq + KClO_3$,* and the two sections separated by any of the following methods:

(*a*) By precipitation (repeated if necessary) by $NH_4OH + NH_4Cl$;

(*b*) By neutralizing, adding excess of an alkaline acetate, boiling and filtering off the basic acetates;

(*c*) By neutralizing (removing H_2SO_4 by $BaCl_2$) and warming with $BaCO_3$ in a small flask, filled to the neck;

(*d*) By nearly neutralizing with $(NH_4)_2CO_3$, boiling, and filtering.

In either case the Al, Cr and Fe''' will be found in the precipitate and the bulk of the other metals in the filtrate: care must however be taken in either case to exclude air or Cl, as Mn and Co tend to be oxidized to triad compounds. The first method is the readiest but the least perfect; it generally suffices for qualitative work. In either case P_2O_5 (and also SiO_2 or TiO_2) is carried down with the Al and Fe, and organic matter interferes to some extent. The basic acetate method effects a better separation, but is tedious and requires more care. When Cr and Zn occur together the Zn always goes down with the Cr if method (*a*) is employed.

Al and Zn require most care for their detection, forming colorless precipitates which are easily masked by others. Fe, Cr and Mn are easily detected without separation by special tests: Fe'' is distinguished from Fe''' by KCNS and K_3FeCy_6. Mn may be separated from all others by solubility of MnS in acetic acid: Ni and Co from all others by insolubility of NiS and CoS in HClAq (diluted with H_2SAq): Al by solubility of $Al(OH)_3$ in KOHAq, not affected by boiling: U by solubility of the sulphide in $(NH_4)_2CO_3Aq$.

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* Or it may be treated with cold dilute HClAq, which dissolves all but NiS and CoS.

METALS PRECIPITATED BY AMMONIUM SULPHIDE ONLY WHEN FOLLOWED BY ACID.

278 The rare elements TUNGSTEN (W^{VI}) and VANADIUM (V^{V}) are usually met with in the form of tungstates and vanadates, derived from WO_3 and V_2O_5, those of the alkalis being soluble in water. They do not fall strictly in either of the preceding groups: the sulphides are soluble in $(NH_4)_2SAq$ as thio-salts, $(NH_4)_2WS_4$ and $(NH_4)_3VS_4$, etc., and remain in solution with part of the Ni after the other sulphides are filtered off: on then faintly acidulating the solution (best with acetic acid) and warming, brown WS_3 and V_2S_5 (and NiS) fall out, and may be tested by the blowpipe.

With $NaPO_3$ in R.F. W gives a brownish-green bead while hot, blue cold (W + Fe gives red); V gives brownish hot, green cold: in borax R.F. V acts as with $NaPO_3$: colors in O.F. are not characteristic. Fused with $Na_2CO_3 + KClO_3$, or with Na_2O_2, complex alkaline tungstates and vanadates are formed, somewhat soluble in water.

TUNGSTEN, in Na_2WO_4Aq, etc., with *HCl* pps white H_2WO_4, slightly soluble in acids, readily in KOHAq or NH_4OHAq. *H_2S* gives no pp. *$SnCl_2$* gives a yellowish pp, turned blue by HCl. *Zinc* + *HCl* reduces solution, giving blue and finally reddish colors.

VANADIUM. Vanadates ($NaVO_3$, Na_3VO_4, etc.) are usually orange like chromates; those of alkalis are difficultly soluble in water containing other salts: all dissolve in HNO_3Aq, and most are decomposed by H_2SO_4, giving yellow solutions, reduced by *zinc* to blue, green, and finally violet.

METALS OF THE ALKALIS AND ALKALINE EARTHS.

279 These comprise all the most positive metals, the sulphides and hydroxides of which are soluble in water (those of Mg sparingly) and turn litmus blue, the normal salts with strong acids being neutral; the two sections are distinguished by the solubility of the carbonates of the alkali-metals, the carbonates of the dyad metals (Ba, Sr, Ca, Mg) being insoluble in water. But in analysis the grouping is somewhat different, as Mg falls with the alkali-metals, its carbonate being soluble in ammoniacal solutions.

CALCIUM GROUP.

Ba, Sr, Ca.

280 The sulphates are insoluble or difficultly soluble in water, $BaSO_4$ requiring about 400,000 parts by weight to dissolve it, $SrSO_4$ over 7,000, and $CaSO_4$ about 400; presence of free HCl greatly increases the solubility. The solubilities of Sr salts are intermediate, in almost all cases, to those of the corresponding Ba and Ca compounds. Ba has the most soluble hydroxide and oxalate, the least soluble chloride, nitrate, sulphate, and chromate.

Soluble carbonates or CO_2 in presence of alkali, precipitate the normal carbonates, which are practically insoluble in water and very slightly soluble in NH_4ClAq, but excess of CO_2 forms soluble acid carbonates, *e. g.*, $CaH_2(CO_3)_2$.*

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*Boiling precipitates the acid carbonate solutions, evolving CO_2, but in presence of ammonium salts the precipitated carbonate may redissolve, see 522.

Na_2HPO_4 pps the phosphates, soluble in HClAq or acetic acid, but reprecipitated as normal phosphates by ammonia.

Pure ammonia gives no precipitates, nor does pure KOH with *dilute* solutions, but if traces of sulphate or carbonate are present, or if exposed to air, a precipitate forms.

Heated on charcoal their salts in most cases leave white infusible residues, which glow brightly on strong ignition.

The more volatile compounds (*e. g.*, chlorides) of these metals color the flame strongly, but some compounds require special treatment, *e. g.*, $BaSO_4$ only reacts after being reduced on charcoal in R.F. to BaS, which is then converted into chloride by HClAq: other non-volatile compounds may be first converted into sulphates by concentrated H_2SO_4 and then similarly reduced. All give highly characteristic spectra.

BARIUM: Ba″: use $BaCl_2Aq$.

281 Most compounds color flame yellowish green (see 280).

$(NH_4)_2CO_3$ pps white $BaCO_3$, almost insoluble in NH_4ClAq, soluble in dilute HClAq, HNO_3Aq, or acetic acid.

H_2SO_4 or solutions of sulphates (*e. g.*, $CaSO_4Aq$) pp white $BaSO_4$, insoluble in alkalis, dilute acids or ammonium salts.

$K_2Cr_2O_7$ pps yellow $BaCrO_4$, insoluble in acetic acid, soluble in HClAq.

H_2SiF_6 pps colorless $BaSiF_6$, very slightly soluble in HClAq.

$BaCl_2$ and $Ba(NO_3)_2$ are insoluble in strong alcohol, and nearly insoluble in *conc.* HClAq and HNO_3Aq.

STRONTIUM: Sr″. Use $SrCl_2Aq$.

282 Compounds color flame crimson (compare Li and Ca).

$(NH_4)_2CO_3$ pps white $SrCO_3$, almost insoluble in NH_4ClAq, soluble in dilute HClAq, HNO_3Aq or $HC_2H_3O_2Aq$.

H_2SO_4 and solutions of sulphates (*e. g.* $(NH_4)_2SO_4$, or $CaSO_4$) pp white $SrSO_4$, slightly soluble in HClAq, insoluble in strong $(NH_4)_2SO_4Aq$.

$(NH_4)_2C_2O_4$ pps white SrC_2O_4, the fresh pp is soluble in an excess of acetic acid, soluble in HClAq.

$SrCl_2$ is soluble, $Sr(NO_3)_2$ insoluble, in strong alcohol.

CALCIUM: Ca″. Use $CaCl_2Aq$.

283 Compounds color flame orange red (compare Sr and Na).

$(NH_4)_2CO_3$ pps white $CaCO_3$, almost insoluble in NH_4ClAq, soluble in dilute HClAq, HNO_3Aq or acetic acid; pp is light and bulky at first, but becomes dense and crystalline on warming.

H_2SO_4 and soluble sulphates (*e. g.*, $(NH_4)_2SO_4$ but not $CaSO_4Aq$) pp white $CaSO_4$ from strong solutions, soluble in hot conc. $(NH_4)_2SO_4Aq$ and in HClAq, slightly in water, insoluble in alcohol which completes precipitation. Alkaline sulphates are preferable to H_2SO_4 as precipitants, on account of the free acid formed by the latter.

$(NH_4)_2C_2O_4$ pps white CaC_2O_4, insoluble in acetic acid, soluble in HClAq: Ba and Sr oxalates being more soluble in acetic acid.

$CaCl_2$ and $Ca(NO_3)_2$ are soluble in alcohol.

MAGNESIUM.

MAGNESIUM: Mg″.

284 Magnesium differs in many ways from metals of the calcium group. The sulphate is soluble in water, the carbonate in NH_4ClAq; the hydroxide is almost insoluble in water (1 part in 500) though readily soluble in NH_4ClAq; its salts do not color flame and most of them are partially decomposed on evaporation of their solutions, forming basic salts.

Heated on charcoal compounds leave MgO, which glows brightly on strong heating: if cooled, moistened with $Co(NO_3)_2Aq$ and again heated strongly, the residue is pink on cooling. All the heavy metals and earths must be separated before Mg can be detected.

285 REACTIONS IN SOLUTION: use $MgSO_4Aq$ or $MgCl_2Aq$. V

NH_4OH pps, incompletely, white $Mg(OH)_2$, soluble in NH_4ClAq as $(NH_4)_2MgCl_4$ or similar double salts, hence no pp falls if much ammonium salt or free acid is present.

KOH pps, almost completely, white $Mg(OH)_2$, insoluble in excess, soluble in ammonium salts; in their presence an excess of KOH must be added and solution boiled.

$Ba(OH)_2$ similarly pps $Mg(OH)_2$; from solutions of the sulphate this is mixed with $BaSO_4$.

Na_2HPO_4 pps white $MgHPO_4$, soluble in acids.

Na_2HPO_4 + NH_4OH (or *$NaNH_4HPO_4$*) pps white $MgNH_4PO_4.6aq$, usually crystalline, insoluble in NH_4OHAq, soluble in acetic and other acids, re-ppd on neutralizing with NH_4OH. Pp forms very slowly.

$(NH_4)_2C_2O_4$, added in excess to a Mg solution, evaporated to dryness and ignited, leaves $MgCO_3$ or a basic carbonate, insoluble in water.

ALKALI METALS.

Na, Li, K (and the compound radical (NH_4)).

286 Nearly all the salts of these metals are readily soluble, hence there are no general precipitants, and they are found in the residual solution after precipitation of all other metals. The salts of K and (NH_4) are generally very similar: Na and Li salts differ from them in many respects, Li having many points in common with the calcium group. Their salts with weak acids usually show an alkaline reaction. All are monads.

The acid tartrates (*e. g.*, $KHC_4H_4O_6$) and the chloroplatinates (*e. g.*, K_2PtCl_6) of K, (NH_4) are difficultly soluble in water, the chloroplatinates insoluble in alcohol, while the corresponding Na and Li salts are readily soluble. Na, Li and K give characteristic flame-colors and spectra. When heated on charcoal most of their compounds fuse readily and are absorbed.

SODIUM: Na′: use NaCl or Na_2CO_3.

287 All compounds color the flame strongly yellow, and give a double yellow line in spectroscope. Either test is very delicate, but traces of Na are found in nearly all substances and always occur in atmospheric dust, so that flame color should not be accepted as a proof of its presence in appreciable quantity unless a persistent yellow color is obtained, the wire used having been previously cleaned by alternately dipping in HClAq and igniting.

There is no satisfactory precipitant for sodium solutions.

LITHIUM: Li′: use LiCl or Li_2CO_3.

288 The flame color is a strong carmine, obscured by large proportions of Na.

Soluble phosphates (*e. g.*, Na_2HPO_4) pp Li_3PO_4 from solutions, more completely when NH_4OH is present.

POTASSIUM: K′: use KNO_3.

289 The flame color is lilac or purplish, but seen through a blue (cobalt) glass appears red-violet. This is the best test for general use. The glass must be thick enough to cut off all yellow (Na) rays, which otherwise obscure the flame color. Li gives a somewhat similar effect with blue glass.

With strong solutions H_2PtCl_6 slowly pps yellow K_2PtCl_6, more completely on addition of alcohol: on drying and igniting Pt + KCl remain. Compare ammonium.

Tartaric acid pps, from strong solutions, white $HKC_4H_4O_6$.

AMMONIUM: $(NH_4)'$ or Am′: use NH_4Cl.

290 Heated in closed tubes compounds either (*a*) sublime or (*b*) are decomposed giving off NH_3. The salts with non-volatile acids are thus decomposed: NH_4NO_3 also breaks up into water and N_2O, NH_4NO_2 into water and N.

All compounds warmed with KOHAq or with $Ca(OH)_2$ give off ammonia, NH_3, with characteristic odor, the gas turning red litmus blue and turmeric brown.

With solutions of NH_4Cl H_2PtCl_6 pps yellow $(NH_4)_2PtCl_6$, closely resembling the K compound, but decomposed by heat, leaving Pt only.

Tartaric acid pps (from strong solutions only) white $HNH_4C_4H_4O_6$.

291 RUBIDIUM (Rb′) and CÆSIUM (Cs′) react very like K, both as to precipitates and flame color; the chloroplatinates are less soluble: in general their salts closely resemble those of K, the properties of the Rb compounds being intermediate to those of the others.

Separation of Metals of the Alkalis and Alkaline Earths.

292 When more than one member of the calcium group is present the group is usually precipitated by $(NH_4)_2CO_3$, after insuring the alkalinity of solution and presence of NH_4Cl. In absence of Ba and Sr (proved by H_2SO_4 giving no pp) Ca may be ppd as oxalate either in alkaline or acetic acid solution; in absence of Ca the other two may be thrown down as sulphates. In the alkaline filtrate Mg is ppd as double ammonium phosphate, or may be separated as $MgCO_3$ after ignition with ammonium oxalate; the fixed alkali metals are best detected by flame-coloration, after expulsion of ammonium salts. Ammonium is tested for in a separate portion, before addition of any of its salts as reagents.

The ppd carbonates of the calcium group are redissolved in acid—usually acetic, from which Ba may be separated as chromate. The chief difficulty is with Sr and Ca; it is not easy to prove the presence or absence of a small amount of either in presence of a large proportion of the other; the insolubility of CaC_2O_4 in acetic acid or of $SrSO_4$ in ammonium sulphate solution may be used. Another system depends on the solubility of $Ca(NO_3)_2$, $CaCl_2$ and $SrCl_2$ in strong alcohol, while $Sr(NO_3)_2$ and both the corresponding Ba salts are insoluble: the ppd carbonates being dissolved in either acid, evaporated, and extracted with alcohol.

293

EFFECTS ON METALS OF HEAT AND THE ORDINARY SOLVENTS.

Use about 1-20 gram of metal in test-tube with about 5 ccs of moderately dilute acid (1 volume conc. acid to 2 water) raising temperature gradually

	Color, etc.	Heated on Charcoal, O.F.	Melts ° C.	Moderately dilute HClAq	Moderately dilute HNO_3Aq	Dilute H_2SO_4Aq	Conc. H_2SO_4	Aqua Regia	KOHAq 10 %	KCNAq	
K	White, soft	Burns, K_2O_4	63	*							K
Na		Burns, Na_2O_2	96	*							Na
Mg	White, mall.	Burns, MgO	750	Sol.	Sol.	Sol.		Readily sol.			Mg
Zn	White, mall. if not crystalline	Fus. ox. (burns) sub.	416				Almost ins. cold, sol. hot evolving SO_2		Sol.	Sol.	Zn
Cd		Fus. vol. sub.	316			Sl. sol.			Ins.		Cd
Al	White, mall.	Fus. ox.	700		Almost ins.	Almost ins.			Sol.	Sol.	Al
Fe	Gray, magnetic	Infus. ox.	1,000 to 1,500	Sol. Fe″	Sol. Fe″ or Fe‴‡	Sol. Fe″			Ins.	Ins.	Fe
Ni	White, magnetic	Infus.		Sl. sol.	Sol.‡	Sl. sol.					Ni
Cu	Red, mall.	Diff. fus. ox.	1,100	† Ins.	Sol.	Ins.				Sol.	Cu
Ag	White, mall.	Diff. fus.	1,040		Sol.‡			Surf. attacked		Sl. sol.†	Ag
Hg	White, liquid	Vol.	—40		Sol. Hg′ or Hg″			Sol. $HgCl_2$		Little or no action	Hg
Bi	Red-gray, brittle	Fus. ox. sub.	270	Ins.†	Sol.			Sol.			Bi
Sb	Gray, brittle		430	Sl. sol.	Ox. ins. Sb_2O_5			Ox. sl. sol.			Sb
As	Gray, brittle	Vol. sub. garlic odor	Vol.	Ins.	Ox. sol. H_3AsO_4			Sol. H_3AsO_4	Sol.		As
Sn	White, mall.	Fus. ox. (sub.)	228	Sol. Sn″	Ox. ins. $SnO(OH)_2$	Sl. sol.	Sol. hot	Sol. $SnCl_4$	Sol. hot		Sn
Pb	Bluish, soft, mall.	Fus. ox. sub.	334	Sl. sol.	Sol.	Ins.	Ins. surf. attacked	Surf. attacked	Sl. sol.†		Pb
Pt	White	Infus.	2,000	Ins.	Ins.		Ins.	Sol. H_2PtCl_6			Pt
Au	Yellow	Diff. fus.	1,250				Ins.	Sol. $HAuCl_4$		Sl. sol.†	Au

Small proportions (*e. g.*, fractions of 1 %) of alloy or impurity often greatly modify the physical properties, especially malleability and color. Larger proportions affect fusibility; the fusing point of an alloy is usually below the mean of those of its constituents.

Generally speaking the less + metals are the less readily attacked by acids, the pure much less readily than impure, and homogeneous alloys less than those which are imperfectly mixed; contact with C or a less + metal (Pt) sets up galvanic action and hastens solution.

Heating, fine division, and roughness of surface facilitate action, rapidity of solution varying with surface exposed.

Moderately concentrated acids are usually most active. Solution may be retarded or prevented by over-concentration or over-dilution of solvent, by liquid becoming saturated with salts produced, or by their insolubility in the acid used, especially if concentrated, thus forming a protective coating over the metal. A mere film of grease (or oxide, *e. g.*, Fe_3O_4) may quite prevent action, and adhering gas-bubbles may greatly retard it by diminishing the effective surface.

When metals dissolve in HClAq or dilute H_2SO_4Aq, H is liberated; when HNO_3 or concentrated H_2SO_4 acts on a metal (the latter requiring heat), H is not set free, but a further quantity of the acid is reduced by the H displaced, forming water and, in the case of H_2SO_4 chiefly SO_2 with more or less H_2S or free S, and with HNO_3 usually NO and other oxides of N or N itself; with very dilute HNO_3Aq NH_4NO_3 is formed in solution or N_2O escapes, the stronger acid gives NO or NO_2, but the products vary with the metal acted upon.

With both HNO_3 and H_2SO_4 the tendency is for the cold dilute acid to form the salts of lower oxidation (Fe″, Hg′), if concentrated to form the higher salts (Fe‴, Hg″) especially if heated; with HCl the lower chlorides are usually formed. But in any case long contact of the solution with an *excess* of metal generally leaves the lower salts or, especially in presence of air, gives precipitates of basic salts. Aqua regia forms the higher chlorides of the metals.

*** Oxidized by water and dissolved as hydroxides, which react with acids.**

† Presence of O (air) enables Cu, Bi, etc., to slowly dissolve in HClAq, and Au or Ag in KCNAq.

‡ Highly conc. HNO_3 renders these metals "passive" and insoluble even in dilute acid.

***Fus.*, *fusible*; *inf.*, *infusible*; *diff.*, *difficultly*; *sl.*, *slowly*; *sol.*, *soluble*; *ins.*, *insoluble*; *mall.*, *malleable*; *ox.*, *oxidized*; *sub.*, *forms a sublimate*; *vol.*, *volatile*; *surf.*, *surface*.**

PART III.

REACTIONS OF THE NON-METALS AND ACID RADICALS.

301 The properties and behavior of the principal non-metals and their compounds are briefly mentioned, followed by the reactions of the salts which they form, these reactions being generally independent of the metallic radicals with which they are combined.

BEHAVIOR OF THE NON-METALLIC ELEMENTS AND SOME OF THEIR COMPOUNDS.

302 The unfamiliar reactions should be verified before using them for purposes of recognition: for comparison the gases may be prepared in small test-tubes by the methods indicated in parentheses.

303 PHOSPHORUS P. On heating in air fuses and burns readily to P_2O_5. Yellow variety inflammable on rubbing, has characteristic odor, soluble in CS_2; red insoluble and odorless, but inflammable on heating.

Special tests: (*a*) P and its compounds, heated with HNO_3, give H_3PO_4, for tests see 348.

(*b*) Any solid compound of P [use $Ca_3(PO_4)_2$] heated in closed tube with Mg, forms Mg_3P_2, and on moistening gives off PH_3 with garlic odor. A flame held at mouth of tube is colored dull green.

304 SULPHUR S. On heating, fuses and burns with odor of SO_2. Ordinary varieties yellow; insoluble in acids; soluble in CS_2; slowly soluble in hot KOHAq (becoming yellow) as $2K_2S_5 + K_2S_2O_3$, reprecipitated by acids, and in KCNAq as KCNS (see 342).

With $KClO_3$ or KNO_3 deflagrates on heating. The precipitated variety is finely divided and passes through filter paper. The plastic variety gradually becomes yellow.

Special tests: (*a*) S and its compounds are slowly oxidized by Br, Cl, or HNO_3 to H_2SO_4, see 345.

(*b*) All S compounds (use any sulphate) fused with Na_2CO_3 on charcoal, in R.F. form Na_2S. Placed on silver and moistened this gives a black stain, Ag_2S. Se and Te compounds act similarly.

(*c*) If fused with $Na_2CO_3 + KClO_3$ all form Na_2SO_4, see 345.

305 CARBON C. Ordinary varieties black. Unaffected by acids, but black varieties are oxidized by $KClO_3$ + conc. HNO_3. Burns slowly to CO_2 on heating in air or O; with $KClO_3$ or KNO_3 deflagrates on heating. Diamond is recognized by extreme hardness.

306 IODINE I. Blackish crystals. Warmed in closed tube volatilizes giving violet irritating vapor, and crystalline sublimate. Slightly soluble in water (brown), readily in CS_2 (violet), and in kerosene, chloroform, alcohol, or KIAq, also in KOHAq (as colorless KIO_3 + 5KI) and KCNAq (as KI + ICN). Traces of *free* I turn starch paste blue, forming starch iodide. Compounds of I do not affect starch or CS_2, and the colors due to free I are removed by ClAq (forming HIO_3 + 5HCl) or by KOHAq, and by *reducing agents*.

307 BROMINE Br. (Heat conc. H_2SO_4 + KBr + MnO_2.) Red irritating vapor, condensing to dark heavy liquid, bleaches litmus. Soluble in water (reddish) and CS_2. With KIAq and starch gives blue color, due to free I.

308 CHLORINE Cl. (Warm MnO_2 with conc. HClAq.) Yellowish gas, suffocating smell, bleaches litmus or indigo instantly. Soluble in water, yellowish. Shaken with KIAq and starch paste traces liberate I giving blue color, removed by an excess. Oxidizes more strongly than Br or I.

Special test for Cl compounds: (*a*) If a bead of $NaPO_3$ is dipped in CuO and heated in O.F. till it almost ceases to color flame, and any compound of Cl is then taken up in the bead and the latter again heated, the flame beyond is colored strongly blue ($CuCl_2$) and fringed with green.

Compounds of Br and I give somewhat similar effects.

309 HYDROGEN H. (From Zn + dilute H_2SO_4Aq.) Colorless, odorless gas, lighter than air; burns, mixed with air or O is explosive.

310 OXYGEN O. (Heat HgO or $KClO_3$ + MnO_2 in small tube.) Colorless odorless gas; reignites glowing splinter. Red fumes if mixed with NO. Absorbed by a solution of pyrogallol in KOHAq, which becomes black.

311 NITROGEN N. (Warm KNO_2 + NH_4ClAq, or NH_4NO_2 or remove O from air by P). Odorless colorless gas, does not burn or support combustion; insoluble and chemically inactive.

312 NITROUS OXIDE, N_2O. (Heat NH_4NO_3.) Colorless gas; reignites glowing splinter; not affected by mixing with NO or O.

313 NITRIC OXIDE NO. (Heat Cu + conc. HNO_3.) Colorless gas, with air or O forms red acid fumes of NO_2. Shaken with $FeSO_4Aq$ gives black $(FeSO_4)_x NOAq$.

314 NITROGEN PEROXIDE NO_2. Red fumes, soluble in water (as $HNO_3 + HNO_2$ reddening litmus); formed by NO and O or air.

315 CARBON DIOXIDE CO_2. (Na_2CO_3 or $CaCO_3$ + dilute H_2SO_4Aq.) Colorless gas, heavier than air, extinguishes glowing splinter. A drop of $Ba(OH)_2Aq$ held in it becomes milky from ppd $BaCO_3$.

316 CARBON MONOXIDE CO. (Solid $H_2C_2O_4$ heated with conc. H_2SO_4 gives $CO + CO_2$.) Burns with blue flame to CO_2.

317 SULPHUR DIOXIDE SO_2. (Heat Cu + conc. H_2SO_4.) Characteristic odor; soluble in water, reddens and then bleaches blue litmus. Reduces ferric salts to ferrous on heating; with H_2S pps S.

318 HYDROGEN SULPHIDE H_2S. (FeS + dilute H_2SO_4Aq.) Characteristic odor; soluble in water; blackens silver or paper moistened with solution of a silver or lead salt. Burns in air with odor of SO_2; oxidizing agents pp S. Reduces ferric salts to ferrous. H_2S and SO_2 decompose each other, giving a pp of S.

319 AMMONIA NH_3. (NH_4Cl + KOHAq.) Gas with characteristic odor; highly soluble in water; gas or solution turns litmus blue; gas gives white fumes with gaseous HCl or other volatile acids, forming salts of ammonium (NH_4).

320 PHOSPHINE PH_3. (CaP + H_2O) is readily inflammable in air (the impure gas spontaneously): the hydride having a characteristic odor (see 303*b*). For ARSINE AsH_3 and STIBINE SbH_3 see 227 and 233, both are readily split up by heat. These three gases are strong reducing agents and give pps (Au, Ag, or Ag_3Sb) when passed into solutions of Au or Ag salts.

321 HYDROCHLORIC ACID, HCl ($NaCl + H_2SO_4$). Pungent acid gas, gives white fumes when breathed upon or in contact with NH_3; very soluble in water, reddens litmus: solution with MnO_2 gives off Cl.

322 HYDROBROMIC ACID HBr (from $5Br + P + 4H_2O = 5HBr + H_3PO_4$) and HYDRIODIC ACID HI ($5 I + P + 4H_2O$) are gases with properties similar to those of HCl, but more readily decomposed by oxidizing agents, the latter by heat alone.

323 HYDROFLUORIC ACID HF. ($CaF_2 + H_2SO_4$) somewhat resembles HCl, distinguished by attacking glass and not affecting MnO_2. (See 336.)

324 GASEOUS HYDROCARBONS: METHANE CH_4. (Heat dry $NaC_2H_3O_2 + NaOH$); ACETYLENE C_2H_2 ($CaC_2 + 2H_2O$), etc., are inflammable in air, burning with a luminous flame to $CO_2 + H_2O$, and explosive when mixed with O. C_2H_2 has a characteristic odor (noticed when a Bunsen burner burns at the base), and gives a pp with an ammoniacal solution of Cu_2O.

325 WATER H_2O: recognized as tasteless liquid, by neutrality to litmus, and by restoring blue color to anhydrous $CuSO_4$. Detected in solids by heating in glass tube.

326 HYDROGEN PEROXIDE H_2O_2 ($BaO_2 + H_2SO_4Aq$) sets free I from $KIAq + FeSO_4Aq$, detected by starch; decolorizes $KMnO_4Aq$ liberating C.

327 SULPHUR TRIOXIDE SO_3, and PHOSPHORUS PENTOXIDE P_2O_5 are white solids which combine very energetically with water, the solutions giving reactions for sulphuric and (meta)phosphoric acids.

328 CARBON DISULPHIDE CS_2, CARBON TETRACHLORIDE CCl_4: volatile liquids recognized by odor and high specific gravity. For other chlorides of P, Si, etc., see 333.

COMPOUNDS OF METALS WITH ACID RADICALS AND NON-METALS.

OXIDES AND HYDROXIDES.

329 The oxides of the heavy metals and earths are nearly insoluble in water (excepting As_2O_3, As_2O_5, CrO_3 which are acid-forming); most of them react readily with acids, forming salts, but some oxides (especially those of Sn, Sb, Fe''', Cr'''

and of Al and the earths), are somewhat difficultly soluble or insoluble after heating. Oxides and hydroxides of the alkalis are highly soluble, of Ba, Sr and Ca less, of Mg very slightly soluble. The oxides of Hg, Ag, Au and the platinum metals give off O on heating leaving metal, the peroxides of Mn, Pb, Na, K, Ba, Cr, Co, Ni, lose part of their O. These peroxides, warmed with HClAq, evolve Cl.

The colors of the more commonly occurring oxides are: *white,* those of the alkalis and alkaline earths generally, Al_2O_3, As_2O_3, As_2O_5; *white to yellowish,* ZnO, CdO, Sb_2O_3, Sb_2O_4, Sb_2O_5, Bi_2O_3, SnO_2; *dark brown to black,* CuO, Hg_2O, Bi_2O_2, Fe_3O_4, Ni_2O_3, CoO, Co_3O_4, Co_2O_3, PbO_2, MnO_2, Mn_3O_4, Bi_2O_2; *brown,* Ag_2O; *yellowish,* PbO, Na_2O_2, K_2O_4; *yellow to red,* HgO; *red brown,* Cu_2O, Fe_2O_3; *red,* Pb_3O_4, CrO_3; *green,* Cr_2O_3, NiO. The colors of many are darker while hot.

Hydroxides are generally more readily soluble in water than oxides, and react more easily with acids. Heated in closed tubes all metallic hydroxides give off water, except those of Ba and the alkalis, otherwise they act like the oxides. KOH, NaOH, and the alkaline earthy hydroxides, with $AgNO_3Aq$, give light brown pps, soluble in NH_4OHAq.

When precipitated from solution they are often lighter in color than the oxides (*e. g.*, $Pb(OH)_2$ is pure white). The proportion of combined water does not always correspond to the "normal" hydroxide, depending often on the conditions of precipitation (less at higher temperatures): some of the less positive metals (Ag, Hg) are ppd as oxides (138) while others form such pps as $SnO(OH)_2$, BiO(OH), etc., and others lose all the combined water on heating, changing color ($Cu(OH)_2$); others like Fe''' lose part only.

The tests are chiefly negative: the insolubility of the heavy metal hydroxides, and the strongly alkaline reaction of those which are soluble, are characteristic, as is the odor of "ammonium hydroxide" and the "feel" of solutions of the fixed alkalis, due to solvent action on the skin. KOH and NaOH solutions set free ammonia from NH_4Cl and pp blue $Cu(OH)_2$ from $CuSO_4Aq$, but the carbonates act somewhat similarly.

330 SULPHIDES: hydrosulphuric acid H_2S: use $(NH_4)_2SAq$, ZnS, and FeS_2.

Sulphides *soluble in water* include those of the alkali and calcium groups, and H_2S, their solutions give black pps (PbS and Ag_2S) with $Pb(C_2H_3O_2)_2Aq$ or $AgNO_3Aq$ and blacken metallic silver; MgS and Al_2S_3 are decomposed by water (MgS partially) forming oxides and H_2S. The normal soluble sulphides (R'_2S) and sulphydrates (R'SH) are colorless, the polysulphides ($R'_2S_{2 \text{ to } 5}$) are yellow in solution, all being decomposed by *HClAq* yielding H_2S (318), polysulphides also pp S. Those *insoluble in water and readily soluble in dilute HClAq* are ZnS, MnS and FeS; *HCl* evolves H_2S from them, and very slowly from most others except As_2S_3 and HgS. All except HgS are decomposed by hot HNO_3Aq, if very dilute this gives some H_2S, but usually yields free S and H_2SO_4 (140).

Heated in open tube, or on charcoal in O.F. all give off SO_2, recognized by odor: in closed tube some (*e. g.*, FeS_2) give free S, and a few (containing water) give H_2S. All give the *sulphur reaction* with Ag after fusing with Na_2CO_3 (304*b*) *even without contact with C or R.F.*

331 CHLORIDES: hydrochloric acid, HCl: use NaClAq.

Nearly all chlorides are readily soluble in water, excepting AgCl and Hg'Cl (Cu'Cl and TlCl) which are insoluble, $PbCl_2$ only slightly soluble, and the chlorides of Bi and the Arsenic group which are decomposed by water, forming free HCl and partly dissolving, leaving insoluble basic salts or As_2O_3.

Chlorides, as a rule, are more volatile than other salts of the same metals, many give oily sublimates on strong heating in closed tubes: those of Sn^{iv}, Ti, As (Si, C, P''', S) are fuming liquids.

All give green flame with $NaPO_3$ bead and CuO (308*a*).

Conc. H_2SO_4 on warming gives off pungent fumes of HCl, except from very dilute solutions: with solids $HKSO_4$ may be used. Addition of MnO_2 then yields Cl (308).

Mixed with $K_2Cr_2O_7$, and warmed with conc. H_2SO_4 chlorides give off brown vapors (CrO_2Cl_2, chloro-chromic anhydride), which may be condensed and dissolved in water, the distillate gives reactions for Cr^{VI}.

$AgNO_3$ with solutions (if not acid should be acidulated with HNO_3) gives a curdy white pp of AgCl, rapidly turned violet by sunlight (see 207), soluble in NH_4OHAq (less rapidly after boiling) re-ppd by HNO_3, nearly insoluble in acids. It must be carefully distinguished from other silver pps (AgCN, AgBr, AgCNS, Ag_4FeCy_6).

Free HClAq, with MnO_2 or other peroxides, evolves Cl.

Evaporated with an excess of HNO_3 all chlorides, except AgCl, leave nitrates (see 352), NOCl and Cl being given off: this must be repeated if the last traces of Cl are to be expelled.

332 DOUBLE CHLORIDES. Among the more important double chlorides are those containing NH_4Cl with a dyad chloride, *e. g.*, Mg, Mn, Zn, which are not precipitated by NH_4OH; and the CHLOROPLATINATES containing $PtCl_4$ and another chloride, usually of a monad metal: the chloroplatinates of K, (NH_4), Rb, Cs, Tl, are nearly insoluble in water or alcohol. They may all be regarded as salts in which Cl is the linking element, see 120.

333 The following CHLORIDES are met with chiefly as fuming liquids decomposed by water forming HClAq and the products indicated: SCl_2 and S_2Cl_2 (yielding $H_2S_2O_3Aq$, SO_2Aq and ppd S), $SiCl_4$ (H_2SiO_3 as a gelatinous pp on boiling), $SnCl_4$ (pps basic chloride), $TiCl_4$ (pps $TiO(OH)_2$), $AsCl_3$ (As_2O_3, ppd by *little* water), $SbCl_5$ (partial pp of SbO_2Cl, etc.), PCl_3 (H_3PO_3 and some P).

PCl_5 is solid, decomposed by a little water to solid $POCl_3$ and HClAq, with more $POCl_3$ forms H_3PO_4Aq and HClAq.

ICl and ICl_3 with KOHAq yield KClAq, KIAq, and KIO_3Aq.

$BiCl_3$, $SbCl_3$ and $SnCl_2$ are solids, also more or less decomposed by water, forming free HClAq and a partial pp of basic chloride (see 502).

334 BROMIDES: hydrobromic acid, HBr: use KBr.

Bromides resemble chlorides in solubility and in many reactions; $PbBr_2$ is less soluble than $PbCl_2$.

Conc. H_2SO_4 on warming, gives off HBr (except from AgBr) partly oxidizing it to free Br; on adding MnO_2 (or $K_2Cr_2O_7$) free Br is readily obtained as brown or yellow vapor; on diluting and shaking with CS_2 the latter becomes brown or yellow from dissolved Br. (See 307 and 322.)

ClAq, added cautiously to neutral or acid solutions, gives free BrAq, best recognized by CS_2.

$AgNO_3$ with solutions (neutral or acidulated with HNO_3) pps yellowish white AgBr, difficultly soluble in NH_4OHAq.

335 IODIDES: hydriodic acid, HI: use KI (see 306).

Iodides generally resemble chlorides in solubilities, but HgI_2 is insoluble in water as well as Hg′I, and the iodides of Cu″ and Fe‴ are unstable, giving CuI and FeI_2 and liberating I.

Conc. H_2SO_4 gives (except with AgI) free I, seen on warming as violet vapor (the H_2SO_4 is partly reduced to SO_2, etc., unless MnO_2 is added); on diluting and shaking with CS_2 the latter becomes violet.

Reactions taking place in neutral or acid solutions:

ClAq, added drop by drop, sets free I, detected by brown color, or by violet solution in CS_2: the color is removed by *an excess of Cl* (forming ICl or HIO_3), by alkalis (forming, *e. g.*, KI + KIO_3) and by reducing agents.

HNO_2 (*nitrous acid, from* $KNO_2 + HC_2H_3O_2Aq$), also $FeCl_3$ and many other oxidizing agents (even $CuSO_4$ but not $HgCl_2$) liberate I. HNO_2, $FeCl_3$, or *ClAq*, used with CS_2 or fresh starch paste, give the most satisfactory tests in doubtful cases. HNO_3 if concentrated, but not when dilute, sets free I.

$AgNO_3$ pps yellowish AgI, almost insoluble in NH_4OHAq.

336 FLUORIDES: hydrofluoric acid, HF: use NH_4FAq and CaF_2.

Fluorides of the alkali-metals, and of the As group, Cr and Ag, are soluble in water, those of Hg″, Fe, Ba and Sr slightly soluble, most others insoluble or difficultly soluble; but most dissolve in HClAq. Those of the alkali-metals, Ca and Al, are the most common. CaF_2 is very slowly dissolved by HClAq and re-ppd by NH_4OH, but is decomposed by hot conc. H_2SO_4.

Conc. H_2SO_4 decomposes all fluorides, evolving HF as pungent vapor resembling HCl, but capable of etching glass: test with watch-glass covering a capsule of platinum, lead or iron. Presence of B or Si (of glass) prevents reaction, forming volatile BF_3 or SiF_4. If much SiO_2 is present or added the SiF_4 may be led into water where it pps gelatinous $Si(OH)_4$ forming H_2SiF_6Aq (fluosilicic acid).

A solid fluoride powdered and heated with *dry fused* $NaPO_3$ on a piece of platinum, placed in an "open tube," gives off HF, dimming the glass above it.

Free HF in solution fumes like HClAq, etches glass, turns Brazilwood paper from red to yellow, and dissolves finely divided SiO_2, volatilizing with it on evaporation as SiF_4: it cannot be kept in glass or porcelain vessels.

$CaCl_2$ pps white gelatinous CaF_2 and $BaCl_2$ pps white BaF_2, from solutions: the former is easily missed; both are very slightly soluble in acids.

337 DOUBLE FLUORIDES. A number of these are known, containing alkali-metal fluorides combined with those of earths or non-metals (*e. g.*, Si, Al, Ti, Sn, as in Na_3AlF_6, K_2SiF_6) which may be regarded as fluosalts.

FLUOSILICATES: fluosilicic acid, H_2SiF_6.

Fluosilicates evaporated with H_2SO_4 give off HF and SiF_4 as white fumes which etch glass. In solutions of H_2SiF_6 NH_4OH pps white $Si(OH)_4$. and $BaCl_2$ pps white $BaSiF_6$, insoluble in HClAq.

338 OTHER BINARY COMPOUNDS. The more familiar HYDRIDES are the hydrocarbons, met with inflammable gases, liquids, or solids: burning to water and CO_2 see 318 to 326. NITRIDES: (for NH_3 see 319) a few metals (Mg, Li which combine directly with N when heated) form nitrides which with water give NH_3 and oxide, or with HCl give NH_4Cl and a chloride. PHOSPHIDE of Ca (CaP) is decomposed by water, giving P hydrides (PH_3, PH_2, etc.) spontaneously inflammable; those of Cu and Sn are met with in alloys, usually hard and brittle if the proportion of P is large (303*a*). ARSENIDES are oxidized by HNO_3 to nitrates and H_3AsO_4 (226–230). CARBIDE of Fe occurs in the ordinary metal, which gives off gaseous hydrocarbons with HClAq and usually leaves free C; some others give off volatile hydrocarbons with water, *e. g.*, CaC_2 (324). SiC (carborundum) is extremely hard, unattacked by acids (even HF). SILICIDE of iron (ferrosilicon) is very hard, scarcely attacked by HClAq, readily by HFAq.

339 CYANIDES: hydrocyanic acid, HCN or HCy: use KCN.

Cyanides of the alkali and alkaline earth-metals are soluble in water and react alkaline, others are insoluble (except $HgCy_2$), but many dissolve in KCNAq as double cyanides. In the dry way they act as strong reducing agents (146); less frequently in the wet way. The free acid and most of its soluble salts are highly poisonous; their solutions have a characteristic odor and taste. Cyanides of heavy metals are decomposed when heated, leaving metal, sometimes mixed with C, and evolving N or CN, the latter burning in air with a red flame.

HCl, dilute *H_2SO_4Aq*, and most acids decompose most simple cyanides, evolving HCN with characteristic odor of almonds, highly poisonous. $HgCy_2$ is only decomposed by *H_2S*.

$AgNO_3$ (from solutions acidulated with HNO_3) pps white

AgCN, soluble in NH_4OHAq; decomposed by fusion ($\dot{=}$Ag + CN) and by boiling with strong HNO_3Aq, otherwise like AgCl. From alkaline solutions no permanent pp may be obtained at first, and none in presence of ammonia.

$FeSO_4$ does not give blue colors at first (but may pp $FeCy_2$ or $Fe(OH)_2$), but on (making strongly alkaline with KOHAq) shaking well and *acidulating* with HClAq, a pp of Prussian blue forms.

Yellow *$(NH_4)_2S_x$* reacts with free HCN and alkaline cyanides to form NH_4CNS; on acidulating this forms HCNS and gives a red color with $FeCl_3$Aq.

In mixtures this is best effected by freeing the HCN with dilute H_2SO_4Aq, causing evolved gas to act on a drop of $(NH_4)_2S_x$Aq held above it, then placing the latter on a glass plate and adding a drop of HClAq and several of $FeCl_3$Aq.

340 DOUBLE CYANIDES. These are of two classes.

(*a*) Decomposed by very dilute HClAq or H_2SO_4Aq, evolving HCN.

These include the soluble double cyanides of alkali-metals with Ag, Hg, Cu, Zn, Ni, Cd, Co″: these are not usually affected by alkalis but on neutralizing their solutions (except Hg″) with acids the metallic cyanides are ppd, those of Zn and Cd are easily redissolved by more acid, AgCy is not affected, the others dissolve with more difficulty. Some (*e. g.*, Au) are not decomposed by acid in dilute solutions.

(*b*) Those not easily decomposed by acids, the Cy and "heavy metal" forming a stable acid radical, *e. g.*, those of Fe″, Fe‴ and Co‴.

341 FERROCYANIDES and FERRICYANIDES are the most important of the latter class, and are derived from the acids H_4FeCy_6 ($2HCy.Fe''Cy_2$) and H_3FeCy_6 ($3HCy.Fe'''Cy_3$). The alkali-metal salts are readily soluble, those of the alkaline earths less, those of heavy metals insoluble; but the latter are decomposed by Na_2CO_3Aq or KOHAq, forming soluble ferro or ferricyanides of Na or K. Dilute HClAq affects them very little, concentrated or hot acids decompose them evolving HCN and forming blue products; evaporation with conc. HNO_3Aq or H_2SO_4 decomposes them completely. Heated on C or in the closed tube they evolve N (sometimes NH_3 or HCN) and leave magnetic residues, in the latter case containing free Fe and C (and KCN in the case of K salts).

Oxidizing agents (especially in acidulated solutions) convert alkaline ferrocyanides into ferricyanides—*e. g.*, *Br*, *Cl*, HNO_3, H_2CO_2. Reducing agents, *e. g.*, $SnCl_2$, SO_2, H_2S, reduce ferricyanides to ferrocyanides.

Their solutions decompose more or less, especially when boiled.

	FERROCYANIDES Use K_4FeCy_6Aq.	FERRICYANIDES Use K_3FeCy_6Aq.
Color of crystals and solutions	Yellow	Orange (blue or green on standing)
$FeSO_4$ (from acid solutions) pps	light blue pp	deep blue pp
$FeCl_3$	Prussian blue	no pp
$CuSO_4$	brown pp	greenish pp
Uranyl acetate	brown pp	Orange
$AgNO_3$	white pp	yellowish pp
Zn salts	white pp	yellowish pp
+ *HClAq*	insoluble	soluble

342 THIOCYANATES or sulphocyanides:

Thiocyanic acid, HCNS: use KCNSAq or NH_4CNSAq.

Most thiocyanates dissolve in water: when heated strongly they are decomposed.

$FeCl_3$, after acidulating, gives blood-red $Fe(CNS)_3$; color removed by $HgCl_2$.

$AgNO_3$ pps white AgCNS, insoluble in dilute HNO_3Aq, soluble in NH_4OHAq.

$CuSO_4$ pps black $Cu(CNS)_2$ with strong solutions, $CuSO_4 + SO_2$ pps whitish CuCNS.

HCl, H_2SO_4 gradually evolve HCN.

343 CYANATES: cyanic acid, HCNO: use KCNO.

Cyanates of the alkali-metals are soluble in water and give a white pp of AgCNO with $AgNO_3$. HClAq and other acids evolve CO_2 with some HCNO (pungent gas), leaving NH_4Cl, etc., in solution.

344 CARBONATES: carbonic anhydride CO_2: use Na_2CO_3 and $CaCO_3$.

Carbonates of the alkalis dissolve in water, a few dyad acid carbonates are soluble, but precipitate on boiling; normal soluble carbonates have an alkaline reaction, acid carbonates are nearly neutral with most indicators.

HCl produces an effervescence with all carbonates, some (Mg, Fe″) requiring heat; CO_2 escapes, recognized by producing turbidity in a drop of $Ba(OH)_2Aq$.

Effervescence without odor on addition of an acid generally indicates a carbonate.

$BaCl_2$ (or any soluble Ba salt) pps white $BaCO_3$ from solutions of carbonates, but only $Ba(OH)_2$ pps free CO_2Aq; pp is soluble in HClAq or acetic acid with effervescence.

345 SULPHATES: sulphuric acid, H_2SO_4; anhydride, SO_3: use Na_2SO_4. (See 304*b*.)

Most sulphates are soluble in water, those of Pb, Ba, Sr insoluble; $CaSO_4$ is slightly soluble, soluble in HClAq; all are insoluble in alcohol, and the slightly soluble ones are precipitated on adding it.

Heated strongly in closed tube, or on charcoal, sulphates of Mg and the heavy metals (except Pb) give off SO_2 and SO_3.

$BaCl_2$ or *$Ba(NO_3)_2$* pps white $BaSO_4$ from solutions; insoluble in dilute HClAq, even on boiling.

$Pb(C_2H_3O_2)_2$ pps white $PbSO_4$; soluble in HNO_3Aq or KOHAq. $BaSO_4$ is little affected by boiling with Na_2CO_3Aq, $PbSO_4$ forms $PbCO_3$.

Free sulphuric acid gives white fumes on evaporating its solutions to near dryness; at this stage it blackens sugar or paper, and evolves much heat if again diluted.

346 SULPHITES: sulphurous anhydride, SO_2: use Na_2SO_3Aq.

Sulphites of the alkali-metals alone are soluble in water; all are decomposed by dilute HClAq or other acids, evolving SO_2.

Br, *Cl* or $K_2Cr_2O_7$ oxidizes them to sulphates.

$BaCl_2$ pps white $BaSO_3$ from solutions, soluble in HClAq.

347 THIOSULPHATES: (hyposulphites) thiosulphuric acid, $H_2S_2O_3$: use $Na_2S_2O_3Aq$.

All thiosulphates are more or less soluble, those of alkali-metals readily. $Na_2S_2O_3Aq$ dissolves AgCl, etc., forming double salts.

HCl sets free $H_2S_2O_3$, decomposed (rapidly on warming) to SO_2 and water, giving a pp of *yellow* S.

$BaCl_2$ gives a pp from strong solutions only: Ag and Pb salts give white pps at first, finally black Ag_2S or PbS.

Iodine is absorbed by $Na_2S_2O_3Aq$, yielding $Na_2S_4O_6$ (tetrathionate) and NaI.

Salts of the THIONIC ACIDS ($H_2S_2O_6$, $H_2S_4O_6$, etc.) and true HYPOSULPHITES (H_2SO_2) are rarely met with: all give the S reactions (304*b*, etc.).

348 PHOSPHATES: orthophosphoric acid H_3PO_4, anhydride P_2O_5: use Na_2HPO_4Aq and Ca_3PO_4.

The pyrophosphates ($H_4P_2O_7$) and metaphosphates (HPO_3) differ in some reactions, but when treated with HNO_3Aq all yield H_3PO_4. Phosphates are not decomposed by heating, except with strong reducing agents, such as Mg or Na (see 303*a*).

Only the alkaline phosphates dissolve in water, all are soluble in HNO_3Aq or HClAq.

From neutral or alkaline solutions *Magnesia mixture* (ammonium magnesium chloride) pps white $MgNH_4PO_4$, insoluble in NH_4OHAq, soluble in acids.

$HNO_3 + (NH_4)_2MoO_4$ pps yellow ammonium phosphomolybdate from all solutions; this pp is of somewhat variable composition, insoluble in HNO_3Aq, soluble in NH_4OHAq, whence magnesia mixture then pps $MgNH_4PO_4$.

If boiled with HNO_3 and metallic tin the metastannic acid formed carries down all the P as stannic phosphate, insoluble in HNO_3.

N. B. Arsenic and silicic acids should be removed before testing for phosphoric.

349 PHOSPHITES (H_3PO_3) and HYPOPHOSPHITES (HPO_3) are derived from the anhydride P_2O_3, and HYPOPHOSPHATES ($H_4P_2O_6$) from PO_2 or P_2O_4. On heating in closed tubes they give off PH_3 and H or P, and on charcoal burn like P. The first two are very strong reducing agents; HNO_3 converts all into H_3PO_4.

350 SILICATES: orthosilicic acid H_4SiO_4: metasilicic H_2SiO_3: anhydride SiO_2: use water-glass (a solution of sodium silicate, $Na_2Si_4O_9$) and feldspar $KAlSi_3O_8$.

Silicates of the alkalis alone dissolve in water; these are decomposed by acids forming soluble silica, on evaporating or boiling, gelatinous $Si(OH)_4$ is deposited. Many others are unaffected by acids, others are partly or wholly decomposed and on evaporation leave gelatinous $Si(OH)_4$; on heating this SiO_2 is formed, insoluble in acids, except $HFAq$; the HF solution is volatilized on evaporation. Precipitated or gelatinous silica dissolves in $KOHAq$ or Na_2CO_3Aq.

SiO_2 and most silicates are insoluble in a bead of microcosmic salt, floating about as a "skeleton."

SiO_2 and insoluble silicates, fused on Platinum with 4 or 5 parts of Na_2CO_3 or $NaKCO_3$, form alkaline silicates, which dissolve in hot water, leaving metallic oxides or carbonates insoluble; on acidulating the solution with $HClAq$ or HNO_3Aq (or heating the fused mass with the acid), evaporating to dryness and treating with hot dilute $HClAq$, SiO_2 remains insoluble.

$H_2SO_4 + HFAq$ decompose finely powdered silicates when heated in a platinum or lead vessel: SiF_4 volatilizing.

351 BORATES: orthoboric acid H_3BO_3 anhydride B_2O_3: use $Na_2B_4O_7$.

Those of the alkalis are soluble, others insoluble or nearly so. Many borates swell when heated, lose water, and finally fuse.

Conc. H_2SO_4 liberates H_3BO_3, from strong solutions this crystallizes out; stirred with alcohol the H_3BO_3 dissolves and on burning it the flame is tinged green. Solids moistened with conc. H_2SO_4 or mixed with $KHSO_4$ and held on platinum wire at base of flame, color it bright green.

From strong solutions of alkaline borates Ba and Ag salts give pps readily soluble in acids.

352 NITRATES: nitric acid HNO_3, anhydride N_2O_5: use KNO_3 and $Pb(NO_3)_2$.

All are soluble in water, except a few basic nitrates (Hg, Bi, Fe'''). Heated on charcoal all deflagrate. Heated in closed tube all give off O on strong heating, those of alkalis leaving impure nitrites, those of heavy metals also give red fumes ($NO_2 + O$ or sometimes HNO_3) leaving oxides: NH_4NO_3 gives $2H_2O + N_2O$.

Conc. H_2SO_4 decomposes all nitrates liberating HNO_3; on adding metallic copper this is reduced forming red fumes, except with very dilute solutions.

$FeSO_4$ reduces HNO_3 to NO (forming ferric sulphates) and with it forms black $(FeSO_4)x$NOAq. To apply as a test:—treat the nitrate, solid or solution, in a test-tube with conc. H_2SO_4, warm gently, allow to become quite cool and pour on it an equal bulk of $FeSO_4$Aq. This floats on the heavier liquid, and at their juncture a dark ring is seen, becoming more apparent if the tube is gently rocked; heating destroys the color.

N. B. Nitrites give this reaction and also deflagrate on charcoal. Chlorates, and large proportions of chlorides, interfere to some extent with the test.

HClAq, added in excess and evaporated, decomposes nitrates leaving chlorides and evolving NOCl and Cl*: a second treatment leaves only traces of nitrate.

Free HNO_3Aq (if not too dilute), warmed with metallic Cu or other metals or reducing agents, gives off NO which forms red fumes with air. With *$FeSO_4Aq$* it gives a brown ring without addition of H_2SO_4. Evaporated in contact with pieces of quill or white wool these become yellow.

Boiled with zinc-dust, or fused with Na_2CO_3 and extracted with water, nitrates give solutions of *nitrites*, and traces may be detected in this way.

353 NITRITES: nitrous acid HNO_2: use KNO_2.

All are soluble in water. Most of the reactions, depending on reduction, are not distinguishable from those of nitrates. NH_4NO_2 decomposes when heated into H_2O and N. Dilute HClAq gives red fumes (NO_2) from dilute solutions of nitrites.

$KI + HC_2H_3O_2$ liberates free I; acetic acid decomposing nitrites but not nitrates, the HNO_2 oxidizing KI: the freed I may be recognized by means of starch paste.

$KMnO_4$ is decolorized by nitrites, but not by nitrates.

354 CHLORATES: chloric acid, $HClO_3$: use $KClO_3$.

All are more or less soluble in water. Heated in the closed tube all evolve O and leave a residue of chloride. Heated on charcoal, or in contact with S, C, KCN or inflammable substances they deflagrate or explode violently.

Conc. H_2SO_4 yields oxides of Cl, dangerously explosive.

Conc. HClAq evolves Cl and Cl oxides with characteristic chlorous odor.

PERCHLORATES react somewhat similarly, leaving chlorides when heated

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*AQUA REGIA (a solution of Cl and NOCl) results when free HCl and HNO_3 act on one another, or HCl on a nitrate, HNO_3 on a soluble chloride, or H_2SO_4 on a mixture of chloride and nitrate. It acts as a powerful oxidizing agent for metals and sulphides.

355 BROMATES (*e. g.*, $KBrO_3$) and IODATES (*e. g.*, KIO_3) act much like chlorates, deflagrating on charcoal and leaving bromides and iodides.

Iodates evolve I with *Conc.* H_2SO_4, and solutions with $AgNO_3Aq$ pp white $AgIO_3$.

356 HYPOCHLORITES: hypochlorous acid, HClO: use NaClO or Ca(ClO)Cl.

All are soluble in water; the aqueous solutions bleach litmus. On heating they yield chlorides.

Dilute acids, even acetic, evolve Cl.

$AgNO_3$ with solutions, gives a pp of AgCl.

SALTS OF ORGANIC ACIDS.

357 Only a few of the more important will be studied. When they are heated more or less charring or separation of C usually takes place, with evolution of CO, CO_2, water, etc.; heavy metals being reduced, alkali and alkaline earthy metals leaving carbonates.

358 ACETATES: acetic acid, $HC_2H_3O_2$ or HAc: use $NaC_2H_3O_2$.

All are soluble in water, Ag and Hg′ acetates the least. On ignition they yield volatile acetone ($CO(CH_3)_2$) with characteristic odor, leaving a carbonate, oxide, or metal.

Conc. H_2SO_4 evolves free $H_2C_2H_3O_2$, with pungent odor.

Conc. H_2SO_4 with solids or strong solutions, mixed with a little alcohol (C_2H_5OH) gives acetic ether (ethyl acetate, $C_2H_5C_2H_3O_2$) with characteristic odor.

$FeCl_3$ gives a red color with solutions, and a brown pp on boiling (142).

359 OXALATES: oxalic acid, $H_2C_2O_4$: use $(NH_4)_2C_2O_4$.

Oxalates of the alkalis are soluble, most others insoluble.

Heated with *conc.* H_2SO_4 the solids give off CO + CO_2, with MnO_2 CO_2 alone is evolved.

$CaCl_2$ or *$CaSO_4$* pps CaC_2O_4 from solutions, insoluble in acetic acid.

$KMnO_4$ is decolorized by hot acidulated solutions of oxalates.

360 TARTRATES: tartaric acid, $H_2C_4H_4O_6$: use the free acid.

When heated, tartrates char and give an odor of caramel, and leave carbonates, etc.

K salts, with strong solutions, pp white $KHC_4H_4O_6$.

Ca salts pp white Ca tartrate, soluble in acids.

$AgNO_3$ pps white $Ag_2C_4H_4O_6$: NH_4OHAq dissolves the pp, but on warming the Ag is reduced as a mirror on side of vessel.

361 CITRATES: citric acid, $H_3C_6H_5O_7$: use the free acid.

When heated they behave much like tartrates, leaving C, etc.

$AgNO_3$, after neutralization, pps white $Ag_3C_6H_5O_7$: soluble in NH_4OHAq, which does not pp Ag.

362 Humic Acid, of somewhat uncertain composition, may be extracted from soils, etc., by Na_2CO_3Aq, or NH_4OHAq (if necessary, that combined with Ca, etc., can be first set free by very dilute HClAq and the $CaCl_2$ removed by washing). The alkaline solution is brown; on acidulating, the humic acid is precipitated brown or black.

Separations of the Acid Radicals.

362 It is not easy to systematically group the acid radicals, as has been done in the case of the metals; and in analysis it is often unnecessary to separate them before detection. Separation is usually effected, when necessary, by taking advantage of the differences in solubility of the Ba, Ag, Pb or Fe salts. Acids are sometimes grouped as "precipitable by silver nitrate," "precipitable by barium chloride," etc., see 418 to 420.

PART IV.

EXAMINATION OF SUBSTANCES OF UNKNOWN COMPOSITION.

401 A portion, as large as convenient, of the substance to be examined should be kept in its original condition, in case the analysis may have to be repeated or some results confirmed: the supply is often limited, and, even if a large amount of material is available, it is preferable to work with moderate quantities.

By making a practice of observing closely the appearance, color, crystalline character, etc., of all substances met with, one can often decide at a glance the probable composition of an unknown salt, or some of the constituents of a mixture; but such indications should be carefully confirmed.

402 In taking up a course in analysis, this part of the work is usually commenced by examining substances of simple composition (*i. e.*, simple salts, acids, hydroxides, or free elements) and determining their nature. It is seldom, however, that substances occur in actual practice which can be assumed to be of simple character, and ordinarily substances presented for analysis should be regarded as of entirely unknown composition, and a close search conducted for all possible constituents: unless it is only desired to decide the presence or absence of some particular radicals.

The system outlined in table II is intended for the simple substances analyzed to give familiarity with the methods: the procedure given is in general the safest but should be freely varied if indications of particular substances seem to justify making a special test at once.

403 For substances of unknown composition, possibly complex mixtures, the system recommended in the next paragraphs is generally very satisfactory and should only be departed from in special cases (as where certain groups have been proved absent) at least until sufficient experience has been gained to allow of other systems being devised. "Short cuts" are often possible, but are not to be recommended to beginners: and it is to be noted that *separation* is generally necessary before attempting a test—to prove the presence of a certain radical it is not sufficient to obtain a precipitate such as it gives with a certain reagent, but it is also necessary to insure the exclusion of all other radicals that can react similarly.

It is self-evident that no satisfactory test can be made for anything which has been added to the substance under examination, or that may have been formed in it; thus it is useless to test for chlorides in a solution prepared by the use of HCl, and the test for sulphates is not conclusive after H_2S has been added to a solution containing any oxidizing agent.

Substances present in fair proportions are usually found in the preliminary tests in the dry way, which should never be omitted with solids; but results thus obtained (especially if negative) should be confirmed by a searching analysis in the wet way.

In the wet analysis the principal danger lies in taking too large or too small a quantity to work with, especially the former—this entails heavy precipitates, bulky solutions, slow filtration, imperfect washing and loss of time generally.

Nearly all the work can be done in test-tubes, using small beakers or flasks if necessary; confirmatory tests can often be made with single drops on porcelain or glass plates or filter-paper.

Great care must be taken to insure the exclusion of foreign matter, keeping beakers, etc., covered if left for any length of time; impurities in reagents must also be considered (136). Reagents should be used in as small quantities as possible, especially the stronger acids and alkalis; if large quantities of these are added, they usually require neutralization later, thus loading the solution with salts which often seriously modify the effects of other reagents on substances present in small proportions.

With due care several operations may be carried on at once; thus the silver and copper group and acids may be tested for while the remainder of the solution is evaporating, or the preliminary blowpipe tests may be made while another portion of the substance is being dissolved.

All precipitates and vessels containing solutions should be plainly labeled if left for any length of time. Brief notes should be made, preferably in tabular form, and all observations and treatment indicated. In reporting results it should be stated whether substances found are present in considerable quantity or in mere traces.

As a rule it is unnecessary, and with solutions it is often impossible, to state in what way the various metallic and acid radicals are associated, but any positive evidence on this point should be noted.

TREATMENT OF LIQUIDS.

404 (*a*) Test with litmus, see 414. Evaporate a few drops to dryness on platinum foil, or on a watch-glass set over vessel of boiling water: observe amount and character of residue, if any. If residue is proportionally large, evaporate more and test in the dry way; the most common phenomena observed are given in 409 to 413.

(*b*) Take a considerable portion and test for metals, see tables II, and III to VI*a*, then test other portions for acids. If strongly acid it is best to decide the nature of the predominating acid first.

TREATMENT OF SOLIDS.

(Except metals and alloys, see 423.)

405 Note closely appearance and general physical properties. Make a thorough test in dry way; the most common phenomena observed are given in 409 to 413.

Treat a very small portion of the fine powder in test-tube or small beaker with 5 to 10 ccs water, warm for some minutes, boil if not readily soluble (see 407). Test with litmus (414).

COMPLETELY SOLUBLE: dissolve ½ to 1 gram in water and proceed as in 404*b*.

NOT ENTIRELY SOLUBLE: boil ½ to 1 gram of fine powder in 10 to 15 ccs distilled water 5 minutes or more, pour or decant off clear liquids: if it does not appear to dissolve at all filter a portion and evaporate a few drops just to dryness on watch-glass or platinum foil; any residue indicates partial solubility.

Treat insoluble portion with dilute HClAq, heating moderately. If entirely soluble, proceed as in 404*b;* if a considerable portion dissolves and action then apparently ceases, pour off, and test residue with more HClAq.

The majority of substances are soluble in hot HClAq if in any acids; a few sulphides, etc., require to be oxidized by addition of HNO_3. If preliminary examination indicates any members of silver group, use dilute HNO_3Aq in place of HClAq.

A residue insoluble in dilute HClAq is boiled with a little conc. HClAq, water added, and warmed. If this fails, use a little conc. HNO_3 or aqua regia.

The use of HNO_3, aqua regia, or of much conc. HClAq is to be avoided if possible. (See 503, 504.) The oxidizing agents are useless with silicates. H_2SO_4 is of little use as a solvent when these fail.

The portions soluble in water and acids may be mixed or tested separately for metals;* the portion finally insoluble is always to be tested separately.

Frequently time is saved by analyzing the water and HCl solutions together, and the HNO_3 or aqua regia solution separately: the latter (*before* mixing, if mixed) should be evaporated and most of the free acid expelled (see 503). In any case a precipitate may fall on mixing some of these solutions. When solutions are tested separately, it is sometimes possible to decide in what way the metals and acid radicals in solid mixtures were originally associated; but the results are often fallacious, as reactions may take place as soon as solution in water commences. As an instance, a mixture of NaCl, $BaCO_3$, HgS and AgCl is separated by the solvents recommended, one simple salt being removed at each step, as they scarcely react on one another. On the other hand, a mixture of Na_2SO_4, $BaCl_2$ and $AgNO_3$ would react on addition of water, giving insoluble $BaSO_4$ and AgCl, so that little information could be thus gained as to the original forms in which the radicals were combined; similarly Na_2CO_3, $Ba(NO_3)_2$ and $AgNO_3$. Frequently the fact that reactions take place on adding water to mixtures is indicated by the change in color or crystalline condition.

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* If to be tested separately, the portion insoluble in each solvent should be well washed before treating with the next.

PRELIMINARY EXAMINATION OF SOLIDS.

406 *Color.*—Compounds of NH_4, Na, K, Si, Ba, Sr, Ca, Mg, Zn, Al are white or colorless unless combined with coloring acids, as are most compounds of As, Sb, Sn, Cd, and many of Hg, Pb, Bi, Ag.

Most sulphides, and the oxides and iodides of heavy metals, are strongly colored.

Most compounds of Cu'', Cr''', Cr^{VI}, Fe'', Fe''', Mn'', Ni, Co, U, have characteristic colors when crystallized or in strong solutions.

But too much importance should not be attached to color when dealing with artificial mixtures, or with substances containing much organic matter, as mere traces of certain organic coloring matters (*e. g.*, coal-tar dye stuffs) will tint large quantities of light-colored materials. Color also varies to some extent with fineness of division.

407 *Soluble in water.* Salts of alkali-metals almost without exception, nearly all nitrates, sulphates, chlorides, ~~bromides~~, ~~iodides~~, ~~chlorates~~, ~~acetates~~, ~~nitrites~~, ~~thiosulphates~~.

Insoluble in water. Most carbonates, phosphates, silicates, sulphites, fluorides and oxalates (of alkali-metals excepted); oxides, hydroxides and sulphides of heavy metals and Mg; simple cyanides of heavy metals (except Hg); sulphates of Ba, Sr, Ca, Pb; chlorides, bromides and iodides of Ag, Hg' (Cu') and Pb; a few oxychlorides, basic nitrates, basic sulphates, and basic salts generally; solid elements; most minerals.

408 *Specific gravity* of salts is generally high with compounds of metals of high atomic weight (*e. g.*, Hg, Pb, Bi, Ba, see 113), and low with those of low atomic weight, Mg, Al, Ca, ammonium, and all the alkali-metals; it varies considerably with the nature of the acid radicals with which they are combined, and is generally low when a large proportion of combined water is present.

409 *Heat a small portion in a closed tube.*

No change occurs on strong ignition	Absence of water or volatile or fusible substances.
Infusible white residue	SiO_2. Al_2O_3, etc.
Changes color	
White or yellow, darker hot	Compounds of Zn, Sn, Pb, Bi.
Red, darker hot	Fe_2O_3, HgO.
Scarlet to yellow	HgI_2.
Blackens permanently	Decomposing oxy-salts leaving oxides of Cu, Fe, Ni, Mn, etc.
with burnt odor	Organic matter.
Gives off water	Water of crystallization, of constitution, hygroscopic moisture, mechanically inclosed, or from decomposition of organic matter.
Gives off gas (*test with litmus and glowing splinter*).	
Supports combustion	O or N_2O from peroxides, nitrates, nitrites, chlorates, etc.
Reddens litmus	
Red fumes, odor of NO_2	Nitrates, nitrites ⎫ of heavy
Odor of SO_2	Sulphates, sulphites ⎭ metals.
CO_2 (pps $Ba(OH)_2Aq$)	Some carbonates and oxalates.
Turns litmus blue, odor of NH_3	Ammonium compounds.
CO, burns with blue flame	Oxalates, organic matter.
H_2S, odor, combustible	Some sulphides.
~~CN, burns, purplish flam~~e	Some cyanides.
Sublimate forms	
Yellow to orange	S*, As_2S_3*, HgI_2.
Reddish brown (black hot) near assay	Sb_2OS_2 (from Sb_2S_3, etc.).
Black near assay	HgS, Te.
Tarry matter, brown or black	Organic substances.
Mirror-like silvery	Hg (nearer assay Cd).
Steel gray	As.*
Oily drops near assay	Many chlorides (Cu, etc.).
White	Compounds of As, Hg, (NH_4) and some of Sb.

[*Confirm the latter by heating with dry Na_2CO_3 and charcoal in closed tube.* Mirror of As or Hg; odor of NH_3.]

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* Vapor yellow or brown.

410 *Heat on charcoal in oxidizing flame of blowpipe.*

Decrepitates	Unequal expansion or inclosed water; alkaline chlorides; many crystals and minerals.
Deflagrates or explodes	Liberation of O from fused substances: nitrates, alkaline peroxides, chlorates, etc.
Odor of SO_2	Sulphides, sulphates, etc.
Powder readily blown away	Escaping gas: usually water or CO_2.
Fuses	Not very characteristic; chlorides, salts of alkalis, etc.
Fuses and sinks	Salts of alkali-metals.
Fuses, gives up water, and resolidifies	Water of crystallization in a highly soluble salt; many sulphates, Na_2CO_3, etc.
Sublimate forms:	
White, remote, volatile	As (Hg, NH_4-, $PbCl_2$).
Nearer assay †	Sb.
Near assay, yellowish, yellow to brown hot	[Volatile in either flame] Pb, Bi.
Very near, white cold, yellow hot; residue glows †	[Non-volatile in O.F.] Zn, Sn.
White infusible residue,† glows	Ba, Sr, Ca, Mg, Al, SiO_2, rare earths.
Black or colored residue	Many heavy metals, Fe, Cr, Ni, Co, Cu, etc.
Magnetic on cooling	Fe (Ni, Co).

411 (*a*) *Mix with dry Na_2CO_3 (or $KCN + Na_2CO_3$) heat on charcoal in reducing flame.*

Sublimate forms	As, Sb, Pb, Bi, Zn, Sn, as above.
Odor of garlic	As, P (compounds other than phosphates).
Reduced to *metallic* beads	Brittle fusible, Sb, Bi.
	Malleable, fusible, bluish, Pb.
	White: fusible Sn, less fusible Ag.
	Red, difficult to fuse Cu.
	Yellow Au.

[† *With white, or light, residues or sublimates near assay—cool, moisten with $Co(NO_3)_2Aq$, ignite strongly in O.F., allow to cool.* Sky-blue infusible, Al, some silicates; blue fused, borates, phosphates, silicates of alkali-metals; light green, Zn; bluish green, Sb, Sn; light pink, Mg.]

(*b*) *Dig out residue and coal that has absorbed flux, crush and test with magnet.* Magnetic, Fe, Ni, Co.

(*c*) *Lay powder on a silver coin, add a drop of water.* Black stain (Ag_2S) indicates a compound of S (Se or Te).

412 (*a*) *Test a small portion of powder in borax bead in O.F., then in R.F.*

[*Substances containing S, As or easily reducible metals should first be thoroughly roasted on charcoal in O.F., beginning at a low temperature, and non-volatile residue treated.*]

Bead is colored: blue Co; green Cr; green hot, bluish cold O.F., reddish (opaque) in R.F. when cold, Cu; brown (violet hot) in O.F , turbid R.F., Ni; violet O.F., colorless R.F., Mn; yellow to red hot, lighter cold, greenish in R.F., Fe; yellowish hot, colorless cold O.F., turbid in R.F., Sb, Pb, Bi, Ni, etc., not characteristic; white and opaque when highly saturated, Zn, Mg, Ca, etc., earths.

[(*b*) See also Mo, U, V, Ti, W, Cb: *if any of these rarer elements are suspected test in* $NaPO_3$ *bead in R.F.: also fuse another portion with* $Na_2CO_3 + KClO_3$, *or with* Na_2O_2 (green or blue Mn, yellow Cr), *dissolve in water, add HClAq in slight excess, then zinc;* gradual change of color of solution: yellow to green, Cr; becomes violet, Ti; blue followed by other shades, Mo, W, V, Cb.]

413 (*a*) *Moisten a little powder with conc. HClAq, take up on clean platinum wire, test in non-luminous flame* (see 149).

Yellow Na; orange-red Ca; crimson Sr, Li; light green Ba (Mo); dull green Sb, P, N compounds; bright green B (in B_2O_3, Tl); strong blue bordered with green, Cu; blue, Pb, As; purplish, K.

(*b*) *Mix powder with a drop of conc.* H_2SO_4 (*or with* $KHSO_4$) *and test at base of flame;* bright green B, borates; dull green H_3PO_4, etc.; bronze green, indistinct, some N compounds.

[*Residue from* (*b*) *may be dried* (*see also 280*), *heated on charcoal in R.F., again moistened with HClAq and tested, see* (*a*).]

EXAMINATION IN THE WET WAY.

414 With liquids, or substances soluble (wholly or partially) in water, test original liquid or aqueous solution with litmus paper (117).

Acid reaction indicates free acid, acid salts, or salts of strong acids with heavy metals. Free acid sometimes results from decomposition of salts of less positive metals by water (502).

Alkaline reaction indicates alkaline or alkaline earthy hydroxides, sulphides, or cyanides, carbonates of alkali-metals, and generally salts of the more positive metals with the weaker acids.

Neutral reaction is met with in comparatively few salts, such as those of the alkali and alkaline earth metals with the stronger acids (see 110, 171).

Solutions of nearly neutral reaction will rarely be found to contain many heavy metals and weaker acids associated.

415 Test a small portion of original substance (unless obviously a "metalliferous" mineral or metal) for *ammonium compounds*, by warming with KOHAq (see 290).

If iron is likely to be present it is also advisable to test solution for Fe″ and Fe‴ by K_3FeCy_6 and KCNS, before oxidation can take place.

GENERAL EXAMINATION FOR METALLIC RADICALS.

416 Take a considerable portion of the solution (see 404, 405) and test for metals (see Table III), test the precipitates obtained in the various groups by the methods given in tables IV, V, and VI. Consult the notes in Part 5. If originally strongly acid it is advisable to decide first what is the predominating acid; if a strong oxidizing agent it may be removed at once, and with substances that deflagrate on charcoal this is generally advisable (see 503*d*).

TESTS FOR ACID RADICALS.

417 Having determined the metals present a little consideration will often show what acid radicals are likely to be present, and which are certainly excluded; *e. g.*, if Ba is found in a mixture readily soluble in HClAq, it is useless to test for sulphates.

Several acids will, if present, have been indicated during the testing for metals—carbonic, silicic, phosphoric; and if arsenious, arsenic, or chromic acids are present, As or Cr will have been precipitated. See also 503 and 418.

The preliminary dry tests will also have given indications as to whether nitrates (or nitrites), chlorates, etc., are present by deflagration, etc., and especially as to the absence of organic acids, other than oxalic; and the failure to obtain a reaction with the sulphur test shows the probable absence of sulphur acids. The test in the $NaPO_3$ bead with CuO may prove presence or indicate absence of Cl, Br, or I compounds. But *negative* results obtained in the dry way should be carefully confirmed.

The following tests are to be made with successive small portions of the original substance, or with the water solution.

They may also be made with the substance after decomposition with Na_2CO_3 (fused, or boiling solution), the insoluble bases being first filtered off; but this treatment is as a rule unnecessary.

418 (*a*) *Add dilute HClAq to a portion of original substance and warm gently.*

Effervescence or evolution of gas: without odor	generally indicates a carbonate [*test evolved gas with a drop of $Ba(OH)_2Aq$*], but may be due to H evolved by some metals.
With odor of H_2S	a sulphide; [*gas blackens lead-paper*] polysulphides also pp free S.
SO_2	a sulphite or thiosulphate (the latter deposits S).
HCN	(like almonds) a cyanide.
Cl	a hypochlorite or peroxide.
Odor of NO_2 (red fumes)	a nitrite (sometimes, with NOCl, from a solid nitrate, or strong solutions on heating).
Cl and Cl oxides (yellow)	chlorates (solid or strong solution, heated).

(*b*) *To the HCl solution add $BaCl_2Aq$:* white pp, insoluble in hot water or dilute acid, indicates a sulphate.

A fluosilicate gives a whitish gelatinous pp ($BaSiF_6$), also insoluble.

(*In presence of any silver group metals use HNO_3Aq and Cl-free $Ba(NO_3)_2Aq$ on a fresh portion, or treat with some excess of HClAq, filter, and test filtrate with $BaCl_2Aq$.*)

Care must be taken to avoid boiling the HClAq, or mistaking the odor of HCl for that of the decomposition products mentioned.

Effervescence should be closely looked for. Bubbles of air escaping from powdered or porous solids may be mistaken for decomposition products; this may be avoided by first adding water, and HClAq only after air has escaped. When but little gas is evolved, no effervescence may be observed.

$HgCy_2$, AgCy and some double cyanides and insoluble sulphides do not react with HCl; contact with zinc and HClAq in some such cases, causes slow evolution of HCN or H_2S.

From solutions not previously acidified $BaCl_2Aq$ may also give a yellow pp from alkaline chromates, white from alkaline carbonates, sulphites, phosphates, borates, fluorides, oxalates, citrates, tartrates, or from the corresponding free acids except hydrofluoric and sulphurous and carbonic: the latter is precipitated by $Ba(OH)_2$. All these are soluble in warm dilute HClAq.

Concentrated hydrochloric and nitric acid give pps with Ba salts.

419 (*a*) *Add dilute HNO_3Aq in slight excess to another portion; warm very gently.*

The same phenomena, effervescence, etc., may be observed as with HClAq (418), with the same inferences; in addition, S sometimes separates from other sulphides. NOCl may be given off by chlorides, and NO by metals or other reducing agents, or free I from iodides, especially if the acid is too strongly heated or insufficiently diluted.

(*b*) *To the clear acid solution add a few drops of $AgNO_3Aq$; if a considerable precipitate forms add somewhat more.*

A small quantity suffices to prove *absence* of chlorides, etc.; if only a very faint cloud forms, make a blank test with some of the HNO_3Aq used.

[*If a precipitate forms wash* it by decantation and treat with NH_4OHAq; if not entirely soluble, filter, and acidulate filtrate with HNO_3Aq; if any has dissolved, it will be reprecipitated.*]

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*Washing of the pp can only be omitted in the proved absence of non-alkaline metals, or with solutions which, before addition of $AgNO_3$, are not precipitated by NH_4OH.

White pp, soluble in NH_4OHAq	($AgCl$) from a chloride (or hypochlorite).
	($AgCN$) cyanide.
	($AgIO$) iodate.
White, soluble in NH_4OHAq (but less easily)	($AgCNS$) thiocyanate.
White, almost insoluble in NH_4OHAq*	(Ag_4FeCy_6) ferrocyanide.
Yellowish white, difficultly soluble	($AgBr$) bromide.
Yellow to yellowish-white, almost insoluble	(AgI) iodide.
Yellowish, soluble*	(Ag_3FeCy_6) ferricyanide.
Black, insoluble in NH_4OHAq (slowly soluble in hot HNO_3Aq)	(Ag_2S) sulphide.
Black, formed slowly	(Ag_2S) thiosulphate.

After being heated the pps are less readily soluble in ammonia.

Where a number of the above radicals are likely to be present, it may be necessary to add excess of $AgNO_3$, and treat the mixed pp with successive small portions of NH_4OHAq, filtering and acidifying each, to effect a partial separation; but in most cases all the necessary information can be gained from a consideration of the results of the tests with $HClAq$, concentrated H_2SO_4, and the iron salts.

The silver salts of these radicals, insoluble in HNO_3Aq, do not answer to above tests: some of the Hg'' salts (*e. g.*, $HgCy_2$), though soluble, do not react, or require an excess of reagent: Hg may be removed by H_2S.

Silver acetate or sulphate is occasionally used to remove some of above radicals, when they interfere with tests to be made subsequently for HNO_3.

By adding $AgNO_3Aq$ to the original or water solution before acidulation there may also be obtained a black pp from sulphides of metals of alkali or Ca group or free H_2S; a yellow pp from phosphates (ortho-), arsenites, or silicates; red-brown from arsenates or chromates; light brown from hydroxides of K, Na, or Ca group (possibly NH_4OH); white (brown on boiling) from carbonates of Na or K; white (redissolving at first, black when acidulated) from thiosulphates; white (redissolving readily at first) from alkaline or Ca group cyanides: but all except AgCy and Ag_2S dissolve pretty readily in HNO_3Aq as well as in NH_4OHAq, and these two dissolve in hot moderately strong HNO_3Aq. Some strong reducing agents (*e. g.*, As_2O_3, phosphites, alkaline tartrates, formates, etc., and other organic substances, especially in presence of free alkali) may give black or gray metallic Ag, easily soluble in HNO_3Aq. From concentrated solutions of acetates or sulphates the Ag salts may pp, soluble on diluting.

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*On warming with NH_4OHAq Fe hydroxide is ppd.

420 (*a*) *Treat a portion with concentrated H_2SO_4; heat, very gently at first, then raise temperature gradually, but not enough to vaporize reagent.*

CO_2, H_2S, SO_2, HCN, etc., may be observed as with HCl or HNO_3, but H_2S or SO_2 may come from reduction of the reagent itself, in presence of certain reducing agents (iodides, metals, etc.) HCN from complex cyanides, thiocyanates, etc., CO_2 from oxalates as well as carbonates.

Strong acid fumes, colorless	HCl, from a chloride HBr, or HF, bromide or fluoride HNO_3 from a nitrate, see below.

[*Confirm HF by etching glass, HCl or HBr by adding MnO_2.*]

Odor of acetic acid	An acetate.
Red to brown fumes	Br from a bromide. CrO_2Cl_2 from a chromate and chloride together.
Yellowish	Cl from a hypochlorite or from a chloride and oxidizing agent together. Cl oxides from a chlorate (often explodes).
Red or brown, with odor of NO or NOCl,	From a nitrate or nitrite (the former only with solids or strong solutions, best after adding Zn or Cu).
Violet vapor	I from an iodide or iodate.

(*b*) *Cool acid liquid, add, without mixing, an equal bulk of $FeSO_4Aq$:* dark ring at contact (due to NO) shows a nitrate or nitrite.

If halogen salts are indicated, test with MnO_2 + conc. H_2SO_4; this indicates chlorides, bromides, or iodides by freeing Cl, Br, or I, and also oxalates by liberating CO_2 (conclusive only if carbonates are first decomposed by dilute H_2SO_4Aq).

421 Special tests should be made for *oxalates* by $CaCl_2$ (confirmed by $CaSO_4Aq$ in acetic acid solution, as HF gives a similar reaction), for *fluorides* by the etching or dimming of glass by liberated HF, for *borates* by flame-coloration, for *phosphates* by ammonium molybdate in nitric acid solution, and for *cyanogen* compounds (if not previously found or proved absent) by $FeCl_3$ and $FeSO_4$ in HCl solution; also for arsenites, arsenates, chromates, etc., if suspected.

It is impossible to give simple directions for the many cases that may arise in which the reactions of one acid radical mask those of another: most of these are solved by the use of other reagents which affect the two radicals differently, but in some cases special difficulties are met, *e. g.*, it is not easy, after recognizing two of the halogen acids as present, to decide whether the third is also present.

PORTION INSOLUBLE IN WATER AND ACIDS.

422 If none of the solvents used (405) had any appreciable effect a fresh portion may be taken here, otherwise the undissolved residue is used. This can only contain a limited number of substances, viz.:

C or S recognized by color, combustibility, or deflagration with $KClO_3$; AgCl,* soluble in KCNAq (or NH_4OHAq); $PbSO_4$,* soluble in KOHAq (or $NH_4C_2H_3O_2Aq$); green Cr_2O_3 or $Cr_2(SO_4)_3$,† red or brown Fe† oxides, brown or black $FeCrO_2$† or $FeTiO_3$,† and white Al_2O_3, $BaSO_4$, $SrSO_4$, $CaSO_4$,† CaF_2,† SbO_2, with SnO_2 SiO_2 and native silicates and aluminates.

A portion of residue should be tested with the blowpipe. Ag, Pb, Sn, Sb, S may be found with soda or KCN on charcoal.

The finding of Pb indicates a sulphate and of Ag a chloride, but the tests are not conclusive in this respect, as the former may be obtained by the oxidation of PbS by aqua regia, and the latter from AgI, AgCN, etc., which are insoluble in HClAq but mainly converted into AgCl by it or by aqua regia.

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*Reducible by the blowpipe with KCN + Na_2CO_3 on charcoal.

†Often found to have gone partially into solution. The oxides of Al, Cr, Fe, Sn, Sb, are nearly insoluble if native or if ignited.

To confirm these acid radicals (if not found otherwise) test one portion of *original* substance with hot Na_2CO_3Aq and another with NH_4OHAq, filter and test the first for sulphate and the latter with HNO_3 for AgCl.

The color may be a sufficient indication of Cr or Fe, confirm in borax bead; they will often be found to some extent in the acid solution. Ba, Sr, and Ca are tested by flame-color after heating on charcoal in reducing flame, and adding HClAq. If Ca is found test specially for a fluoride.

SiO_2 (unless from the decomposition of silicates) is often hard enough to scratch glass, similarly native Al_2O_3 and many native silicates. The silicates and SiO_2, after drying thoroughly, effervesce when fused with freshly fused Na_2CO_3. Heated with HFAq and H_2SO_4Aq in a platinum capsule they dissolve, and on evaporation the Si is volatilized.

To test systematically, free a portion from Ag and Pb by KOHAq and KCNAq, and from C and S by burning. Dry the residue and fuse with about 4 parts by weight of Na_2CO_3 or $NaKCO_3$ and one of $KClO_3$ on platinum foil for some time. Treat the residue with water, boil two or three minutes and filter. Solution may contain (beside carbonate and chloride) the Cr, F, SO_4, and more or less of the Al, Sn, Sb, SiO_2 in the form of alkaline salts. Acidulate, evaporate to dryness, heat gently, treat with dilute HClAq: SiO_2 remains insoluble, test in $NaPO_3$ bead. Treat the filtrate for other radicals mentioned.

The residue from fusion, insoluble in water, may contain Fe, Al, Ba, Sr, Ca (Sb, Sn); treat with HClAq and test.

Some alloys of Au + Ag containing over ⅓ gold are insoluble in aqua regia: these are fused with two or three parts by weight of Ag (or Cu), rolled out and the Ag (or Cu, removed, with other metals) by HNO_3. Alloys of Au + Cu, rich in gold, are not attacked by HNO_3, but dissolve in aqua regia (see 423).

TREATMENT OF METALS AND ALLOYS.

423 Note color and whether malleable, brittle, or readily fusible; test with magnet. (See 293.)

Metals present in any considerable proportion can be detected by the blowpipe (see 410).

If brittle, powder about a gram; if malleable, cut up or roll out thin, so as to expose a sufficient surface to solvents.

Treat a small portion (about ¼ gram) with 10 to 15 ccs of moderately strong HClAq and another portion with moderately strong HNO_3Aq: keep somewhat below the boiling point for some time. Most alloys are attacked by one or the other.

(*a*) If HClAq dissolves it readily, Bi, Sb, Pb, Hg, Ag, Au Cu are not present in large proportions: proceed to test for metals in solution.

(*b*) If HNO_3Aq dissolves it readily and completely, Al, Cr, Sn, Sb, Au, Pt, are not present in large proportions: evaporate down twice with HClAq (503) and test for metals, and also for H_3PO_4 and H_2SO_4, indicating P and S in the alloy.

(*c*) If HNO_3 forms a white deposit, insoluble in hot water or dilute HNO_3Aq, Sn or Sb is present: filter, wash pp well with hot water. Treat filtrate as in *b*. Digest pp with a few drops of KOHAq and some yellow $(NH_4)_2S_x$Aq, at a gentle heat: add some water, warm and filter if necessary: acidulate filtrate with HClAq and test pp for Sn, Sb, and As, see Table VI, Arsenic Group.

The white pp always retains As and P if present.

(*d*) If insoluble in either acid treat with aqua regia: evaporate as in *b*, dilute, filter off AgCl if necessary, and test for Au and Pt in the concentrated solutions (251), then for other metals. (See also 422.)

CASES REQUIRING SPECIAL TREATMENT.

424 In cases where a number of acids require to be tested for, and heavy metals are present, the latter may require to be removed: it is then advisable to boil the powdered solid or a strong solution with a strong solution of Na_2CO_3 for 5 or 10 minutes, filter, and test for acids in the filtrate. This is rarely necessary in the test for sulphates, nitrates, or phosphates, and is useless with carbonates and sulphides. It is not always applicable with Hg salts: when Hg or the As group interfere it is preferable to acidulate with HCl and remove metals with H_2S before testing for acids.

Silver, in the form of chloride, bromide, iodide, or in cyanogen compounds, barium and strontium in the form of sulphate, and most of the silicates require fusion with Na_2CO_3 or $NaKCO_3$ to effect decomposition, the filtered water extract being tested for acids.

It must be remembered that certain acid radicals may be decomposed by this treatment, usually by oxidizing or reducing one another: chlorates, chromates, nitrates, etc., decomposing cyanides, sulphides, and organic radicals, and being themselves reduced.

425 In *furnace products* and silicates generally the treatment in 424 or 430 is to be applied, unless HClAq effects decomposition: no tests should be made for nitrates or any organic acids, but phosphates, sulphides, carbonates, chlorides, and sulphates should be looked for.

426 *Complex cyanides:* these often require special treatment: the solution or solid is evaporated down with H_2SO_4 or conc. HNO_3 and residue tested for metals: Fe, CO, etc., thus found may have been present in the acid radical of a complex cyanide. For acid radicals the treatment in 424 is adopted and the tests below applied.

If HCN has been evolved at any stage test the faintly acidulated solution with $FeCl_3$ and $FeSO_4$: if no coloration is obtained test carefully for simple cyanides. If $FeCl_3$ gives a blue color take a fresh portion, make faintly acid with HClAq, add $FeCl_3Aq$ (blue pp = ferrocyanide), warm a few minutes, allow to stand, filter (repeatedly if necessary) till clear (red color of solution = thiocyanate), add $FeSO_4Aq$ or SO_2 (blue = ferricyanide), filter till clear, make alkaline with KOHAq, shake well' acidulate with HClAq, blue color (Prussian blue from ferrocyanide formed) indicates a simple cyanide. Zinc interferes with the tests for ferro and ferri-cyanides, it cannot be completely removed from cyanide solutions by Na_2CO_3. Hg should be removed by H_2S before making above test. It must be remembered that ferrocyanides are converted into ferricyanides by oxidizing agents, reducing agents reversing the change.

427 Quartzose *ores* (gold ores, etc.) and vein matter containing small proportions of metalliferous minerals The most commonly occurring of these minerals are pyrite (FeS_2), chalcopyrite ($CuFeS_2$), magnetopyrite (Fe_7S_8), arsenopyrite (FeAsS), galena (PbS), blende (ZnS), with other more complex sulphides, arsenides, antimonides, etc., silver-bearing sulphides, Te and tellurides of Ag or Pb, and from oxidized ores green or blue carbonates of copper, red, brown or black oxides of iron, black MnO_2, free gold, silver, or AgCl. Cinnabar (red HgS) and free S are sometimes found.

It in particles of moderate size, these can often be picked out and recognized individually by physical properties, even when in such extremely small proportions as to be easily missed in a wet examination of the whole mass. When the proportion is small the ore should be crushed moderately fine and "horned" or "panned" by washing under water in a small porcelain dish to remove the lighter material and concentrate the heavier sulphides, etc. By spreading the "concentrates" in the dish, and washing down with a fine stream of water from wash bottle any free gold can usually be seen at edge, unless covered by a large proportion of sulphides. To detect the gold the sulphides may be removed from a portion of concentrates by heating with hot HNO_3, and washing repeated. Another portion of concentrates is treated with HNO_3 or aqua regia and tested for non-alkaline metals (405).

Or the S and As are roasted off by heating and stirring in an open dish till there is no further odor of SO_2, the residue is digested for an hour with warm Br water which is filtered off, boiled to remove free Br, and tested for Au by absorption in paper and burning (245) and for Cu by flame-color, etc. (216): the residue is washed free from Br and warmed for some time with KCNAq; on filtering off and acidulating the latter a pp of AgBr shows the presence of silver.

For Au and Te the concentrates are put in a porcelain dish with water enough to cover them, a few grams of sodium amalgam are added and stirred in, when a purple color in solution indicates Te (247): the amalgam is then rubbed and ground well with ore, the latter is washed off into another dish: the amalgam is dried, Hg evaporated off at a low temperature, the residue may then contain Au and Ag, fuse or cupel and test. Or treat the amalgam with hot HNO_3Aq, the brown residue contains Au, fuse and test. The sulphides from which the amalgam has been removed are generally easily attacked by acids, and may be tested for heavy metals, Hg excepted.

If milled, or crushed in an iron mortar, the ore may contain metallic iron (or Fe + Cr) from wear of castings; this is best removed at first by a magnet, which may also take up some of the Fe minerals mentioned.

The lighter gangue, or a portion of it, is first treated with hot HClAq which may dissolve carbonates or other compounds of Ca, Mg, Fe, Mn, Cu, leaving SiO_2 and silicates of Al, Mg, Ca, etc. (such as feldspar and mica), sometimes $CaSO_4$, $BaSO_4$, $PbSO_4$, or CaF_2, which should be tested for.

428 With highly *sulphuretted* or *arsenical ores*, or any carrying but little silica or earthy minerals, the preliminary concentration (427) is omitted and the material attacked at once by HNO_3, aqua regia, $HNO_3 + Br$, or $HCl + KClO_3$; or it is roasted and treated with HClAq, etc., as in 405.

429 The presence of considerable quantities of *organic matter* often makes it impossible to test for the ordinary (inorganic) acids and bases. Several methods may be used to remove it.

(*a*) It is burnt off by heating in air in a porcelain or platinum vessel: volatile substances may be lost by this treatment.

(*b*) It is oxidized by heating with conc. HNO_3 (or $HNO_3 + H_2SO_4$), evaporating to dryness, and redissolving in dilute acid.

(*c*) The mixture is dialyzed through parchment paper or an animal membrane, the crystallizable substances passing through into the water, which is then evaporated and tested.

(*d*) Organic matter of some descriptions can be removed by solvents, *e. g.*, ether and gasoline are solvents for fats, alcohol for resins, CS_2 for rubber, etc.

Thus paints in oil may be treated with HNO_3 and the floating oil removed by filter-paper; or the oil may be dissolved out by gasoline or ether and the residue tested. Samples of metals and alloys are often coated with grease or oil, removable by gasoline or ether.

No mention has been made of the means of detecting or separating the many organic substances frequently met, *e. g.*, the alcohols, ether, chloroform, acetone, phenol (carbolic acid), glycerine, the sugars, etc.; many of these are readily recognized by odor, taste, specific gravity, volatility (some of the lighter liquids producing intense cold by evaporation), viscosity, combustibility, etc., but in mixtures their detection is often a matter of difficulty.

430 *Alkali-metals in silicates* which resist HClAq cannot be detected by the usual methods, and it is useless to test for them after fusion with carbonates (424). The fine powder may be mixed with HFAq and H_2SO_4Aq in a platinum or nickel dish, warmed and stirred for some time, and then evaporated (under a hood) as long as fumes rise; Si is thus expelled as SiF_4. The residue is heated with HClAq, filtered, and solution tested for alkali-metals, and other metals if necessary.

PART V.

NOTES.

REFERRING TO TABLES III to VI.

N. B. Whenever a filtration is directed in the tables a horizontal line is drawn, followed by a vertical; the latter separates the directions for treating the solid and the soluble portions. The previous treatment of any portion at any stage can always be found in the space above. When no precipitate forms filtration is omitted.

501 Reagents should, at all stages, be added cautiously and little by little, noting the effect of each addition, unless the amount necessary is approximately known.

It is advisable to make a point of remembering the name and formula of each reagent added, and invariably, before adding a reagent, to consider the object of using it and what its effects may be—*i. e.*, what compounds it can possibly form with the bodies present under the present conditions, and also what effect it may have on other reagents to be added later; and also whether it will interfere with subsequent tests, *e. g.*, whether it may introduce some radical which will have to be tested for in the same portion of substance, and thus prevent its detection.

It must be borne in mind that, in precipitating, secondary products always remain in solution, and their presence may have to be considered in all subsequent tests.

Precipitation should be made as nearly complete as possible; this may be insured by testing a small portion of the filtrate with a further portion of the precipitant, if no additional precipitation is observed after waiting a reasonable time it may be considered as complete for qualitative purposes.

Precipitates should invariably be carefully washed before testing. For qualitative purposes two or three washings are generally sufficient; if it is necessary to take greater precaution, a few of the last drops of the filtered wash-water are tested, usually for Cl or some radical present in the last solution; washing is stopped when practically free, or if the medium was acid the washing is carried on till water is neutral.

The object of precipitation and filtration is to effect a separation of two radicals or groups from one another, or one from all associated substances: the two last precautions insure the approximate completeness of the separation.

The filtrate and the first wash-water are usually mixed and tested—they contain by far the greater part of the soluble matter—but the pp must be washed further, or the small amount of soluble salts contained may interfere with the tests to be applied.

When one metal is evidently present in very large proportion, it is a good plan to get rid of it, or most of it, at the outset, if that is practicable. For instance, in analyzing an impure lead, a large amount of it should be dissolved in HNO_3Aq, and the bulk of the Pb removed by H_2SO_4; after evaporation and redissolving, a solution is obtained containing a fair proportion of the other constituents, which otherwise might be missed. Similarly with an amalgam the bulk of the Hg can be expelled by heat before commencing the analysis.

SEPARATION INTO GROUPS.

502 From too concentrated a solution many salts may be precipitated on addition of HCl, being less soluble in acid than in water.

On adding water a white pp may form of basic chlorides (oxychlorides) of Bi, Sb, Sn, or basic nitrates of Bi or Hg, such pps will generally redissolve on the addition of HClAq (§I), or they may be separated by decantation and then either tested separately or treated with a little conc. HClAq and added to main solution.

503 (*a*) Effervescence on addition of HClAq, if without odor, indicates a *soluble* carbonate, with odor of SO_2 a sulphite or thiosulphate, of H_2S a sulphide, of HCN a cyanide, of Cl usually a hypochlorite (see 418).

(*b*) If HCl were used to effect solution of a solid none need be added here, but if solid were dissolved partly in water and partly in HClAq a pp may form on mixing the two portions; this may be a silver group chloride, or a carbonate, sulphate, etc. In such cases add more HClAq till decidedly acid; if pp does not dissolve on warming it is probably a member of the silver group or a sulphate of Ba, Sr, or Pb.

(*c*) *Alkaline* solutions on being *neutralized* by HClAq may precipitate various compounds: those most commonly met with are hydroxides, most of which redissolve readily on addition of more acid, sulphides of As, Sb. and Sn (strongly colored, the first two redissolving with difficulty, that of As being nearly insoluble), and cyanides, some of which are readily soluble, some insoluble, while in special cases other salts and insoluble acids or anhydrides may be formed.

For instance, from a solution containing free KOH or NaOH there may be precipitated hydroxides or oxides of Pb, Sn (As), Sb, Al, (Cr'''), Zn, $PbSO_4$ and almost any other lead salt, sulphides of As, Sb, or Sn. From ammonium sulphide solution there may fall free S, and sulphides of As, Sb or Sn^{IV} (Ni or Cu): from K_2S or Na_2S solution those of As, Sb, Sn'' or Sn^{IV} (see 244) and Hg: from ammoniacal solution may fall hydroxides or cyanides of Cu, Cd, Zn, Ni, Co, (Mn); As_2S_3 or As_2S_5, S, AgCl or AgCN: from KCN solution may fall AgI, AgBr, AgCN, Ag_2S, CuS, NiS, CoS, and cyanides of almost any other heavy metals (except Hg, Pb or Bi), most of the cyanides being readily soluble in HClAq: from solutions evolving SO_2 may fall As_2S_3, S, Ag_2S, $PbSO_4$: carbonates may give precipitates of As_2S_3, and $(NH_4)_2CO_3$ may give AgCl, AgCN, As_2S_3.

On standing, gelatinous H_4SiO_4, or some other form of silicic acid, may separate out.

(*d*) If a large amount of HNO_3 or aqua regia has been used, or if any strong oxidizing agent is present (*e.g.*, a chlorate, nitrate, chromate, permanganate, SO_2, Cl, Br, I), indicated by odor of ClO_2, Cl, NOCl, SO_2, etc. (chromates are indicated by yellow color of solution, confirm by neutralizing with NH_4OH and adding $HC_2H_3O_2$ and $Pb(C_2H_3O_2)_2$; permanganates by purple color and ozone-like odor of solution, and evolution of Cl when evaporated with HClAq); it is best to boil down add some conc. HClAq, evaporate to complete dryness and redissolve in dilute HClAq before proceeding further. These oxidizing agents, if allowed to remain, will react on the H_2S next to be added, not merely decomposing it and requiring the addition of large quantities, but forming H_2SO_4, S, and troublesome decomposition products. See 504.

As much lead as possible should be removed by HCl, using a slight excess and cooling, but pp is never complete: the dissolved $PbCl_2$ falling as PbS in copper group.

504 If H_2S water is used it should be clear and should smell strongly of the gas: in this case previous dilution is unnecessary if the H_2SAq is added in sufficiently large proportion.

Gaseous H_2S may be used, but in this case the solution must be considerably diluted first.

If solution is neutral Fe, Ni, Co, Zn, may be thrown down, by the H_2S; if alkaline these and Mn will be precipitated, but As, Sb, and Sn will fail to pp.

If much free acid is present Cd may fail to pp, and Pb if acid is in great excess, both causing trouble and confusion by being precipitated later on in other groups.

From strongly acid solutions Pb may fall at first as brick-red $Pb_3S_2Cl_2$, becoming black on dilution and warming with more H_2S.

Any very large excess of acid is best got rid of by evaporation or *partially* neutralized by NH_4OHAq.

It must be remembered that H_2S, in precipitating sulphides, *sets acid free* (see 505 and 138): if a very heavy pp forms the proportion of acid generated may be so large as to interfere with precipitation of the last traces of metal.

There need be no fear of adding this reagent in too great excess, except from the inconvenient bulk of liquid resulting, as it has no appreciable solvent action on the sulphides, and is easily expelled, but it is desirable not to make the bulk of liquid too large, as this increases time of filtration and evaporation (506 to 508).

Arsenic, if present in the pentad form, may be missed if solution is not heated to 70° and an excess of H_2S added. If As^V is suspected it can be reduced to As''' by adding SO_2Aq and *boiling off the excess of* SO_2 before adding H_2S. The SO_3 formed may pp Ba or Sr as sulphate in this group.

Milky white S, so finely divided as to pass through a filter, is ppd by the action of H_2S on oxidizing agents (*e.g.*, $FeCl_3$, H_2CrO_4, $HMnO_4$, Cl, HNO_3, etc., which are thereby reduced to $FeCl_2$, $CrCl_3$, $MnCl_2$, HCl, NO, etc.): some of these may oxidize part of the S to SO_3 and thus pp Ba or Sr from the solution; most of these may be removed by evaporating with HClAq (503); Fe''' is reduced to Fe'' by heating with SO_2, the excess of which must be expelled, as $SO_2 + 2H_2S$ equally pps S. Occasionally the S is ppd in the plastic form.

505 Test part of filtrate *immediately* by adding an excess of H_2S; if gas is used, dilute still further; if very strongly acid, it may be advisable to partially neutralize first, but care must be taken to avoid complete neutralization, as it may be impossible to correct this by subsequent acidulation, as in that case the iron group metals will pp, and NiS and CoS are, when once formed, insoluble in HClAq.

If amount of pp II is excessive, it is possible that too much of the original substance has been taken; in such a case, the filtrate may be divided at this point, and the pp mixed and then divided for treatment.

506 H_2S must be boiled off if it is proposed to pp Al, Fe and Cr separately from Ni, Co, and Zn (see 516 and table for pp III and IV: alternate method).

If H_2S is not expelled, NH_4OH pps FeS, NiS, etc., here; it also retards oxidation of Fe'' by HNO_3 (507).

If HCl gives no pp and H_2S none but S (provided in the latter case that H_2CrO_4 and $HMnO_4$ are absent or have been reduced by evaporation with HCl), a fresh portion may be taken for treatment at this point.

507 Evaporation to dryness may in many cases be omitted (see 508), but after treatment with H_2S it is desirable to concentrate and reduce bulk after the necessary dilution in § II.

After treatment with H_2S iron is present as Fe''; this must be peroxidized by HNO_3, unless it is intended to add NH_4OH and then $(NH_4)_2S$ without an intermediate filtration (516); for Fe'' salts are not completely ppd by ammonia as are those of Fe'''. BrAq may be used in place of HNO_3 if it is merely desired to peroxidize iron.

508 Evaporation to complete dryness with the addition of conc. HNO_3 is generally advisable in the presence of phosphates, borates, oxalates, fluorides and silicates if NH_4OH gives a pp at this point (511), and always in presence of organic matter, as the latter retards or prevents precipitation of Fe (Al and Cr) by NH_4OH. By this treatment borates, oxalates and fluorides are largely decomposed, while soluble silicates and organic matter are decomposed, leaving SiO_2 and C when further heated; if these are not removed, such substances as CaF_2, $Si(OH)_4$, CaC_2O_4, etc., will be ppd by NH_4OH, and will subsequently come down in the place of $Al(OH)_3$, for which they may be mistaken. Phosphoric acid is not removed, but all P compounds are converted into orthophosphates (H_3PO_4 salts) by boiling with HNO_3.

509 A pink color of solution changing to blue near dryness indicates Co, green leaving yellowish residue Ni, green or violet to green Cr, yellow to brown or black Fe, faint pink to brown or black Mn. A white residue indicates absence of these metals; if residue is light in color, fuses easily, and dissolves readily in water, there is probably an alkali or alkaline earthy metal, or Zn; the taste of the water solution often gives a clue to the nature of the predominating substance. If no residue remains on ignition, these substances are excluded; and a readily volatile residue indicates ammonium if none of its compounds have been added—test original substance. Ferro and ferri-cyanides, if previously overlooked, usually leave blue residues at this point; these should be again moistened with conc. HNO_3, dried and ignited, and if necessary this treatment repeated, after which HClAq usually dissolves the residue as $FeCl_3$.

510 If heating is carried too far, a portion of the residue (Al_2O_3 white, Cr_2O_3 green, Fe_2O_3 red or brown to black, besides white SiO_2 and black C) may be rendered insoluble in HClAq, but if silicates or organic compounds are present, moderate ignition is necessary (leaving white SiO_2 or black C).

511 Phosphoric acid must invariably be tested for here, after removal of arsenic and silicic acids, which also give yellow pps or colors with $(NH_4)_2MoO_4$, but less readily; a yellow *color* without pp is not sufficient proof of presence of H_3PO_4; too much HCl interferes with test. The test is best made by pouring about 1 cc of the solution *into* 2 or 3 ccs of the molybdate solution.

If H_3PO_4 is present *and* NH_4OH gives a pp, a special treatment will probably be necessary for pp III.

(*b*) This somewhat complicated special treatment (see table for pp IIIA) may often be avoided by adding a sufficient quantity of $FeCl_3Aq$ at this stage (after first testing for Fe in a special portion—if amount of Fe already present is large and of H_3PO_4 small, no more $FeCl_3$ need be added), the phosphoric acid being carried down combined with $Fe(OH)_3$ on addition of NH_4OHAq, as a basic ferric phosphate $FePO_4.xFe(OH)_3$. The necessity for some special treatment is owing to the precipitation of Mg and Ca (Ba and Sr) with the Fe, Cr and Al; the other metals act much the same whether H_3PO_4 is present or not, the phosphates and hydroxides being similar in solubilities, except that $FePO_4$, $AlPO_4$ and $CrPO_4$ are nearly insoluble in acetic acid and are very slimy and difficult to filter.

512 The amount of NH_4Cl necessary depends chiefly on that of the Mg and Mn to be retained in solution as double chlorides on addition of ammonia, and partly on that of the Ni, Co, and Zn. If solution has not been evaporated to dryness, it usually contains much HCl, which with NH_4OH may yield sufficient NH_4Cl. Too large an excess of NH_4Cl may prevent subsequent precipitation of calcium group.

513 Too great an excess of NH_4OH dissolves $Al(OH)_3$ appreciably (570). The gelatinous and almost transparent colorless pp of $Al(OH)_3$ must be closely looked for and a few minutes allowed for it to separate; it usually floats, owing to entangled CO_2.

514 The ammonia used must be nearly free from carbonate; if exposed to air, CO_2 is absorbed, so that Ba, Sr, and Ca may be ppd here and subsequently missed.

By exposure MnOaq and CoOaq are oxidized to Mn_2O_3aq and Co_2O_3aq, becoming insoluble in NH_4ClAq and therefore falling in pp III.

There is also a great tendency for the dyad metals (Mn, Zn, etc.) to form somewhat stable salts (ferrites, chromites, aluminates: $R''O.R'''_2O_3$, analogous to the "spinels") with the sesqui-oxides of this group; if much Fe is present there is a special tendency for Mn (and Co) to be carried down with it (apparently as $MnO.Fe_2O_3$), Ca and other dyads are also carried down, whence the precaution with large dark pps to redissolve in HClAq and re-pp with NH_4OHAq (see 512), which frees the pp from most of the dyad metal, the filtrates being added to the main filtrate ℨ IV. The rapid darkening of the pp on filter is an indication of the presence of Mn (or Co).

In presence of Cr there is a special tendency for Zn to accompany it in the pp as $ZnO.Cr_2O_3$; the Zn is very imperfectly separated from the Cr by reprecipitation; Mg is similarly carried down by Cr, unless the proportion of NH_4Cl is large.

The ppd hydroxides (and especially the phosphates) are gelatinous, filtration is tedious, and separation from soluble matter imperfect unless performed hot and pp washed with hot water. If pp is large, it must be allowed to settle, clear liquid decanted and washing done largely by decantation; a long boiling prior to filtration makes it even more gelatinous.

The Cr^{vi} and Mn^{vii} of chromates and permanganates are not precipitated by NH_4OH, unless these are previously decomposed by HCl or $HCl + H_2S$, presence is indicated by color of solution; if allowed to remain they are ppd by $(NH_4)_2S$. Similarly the Fe of undecomposed ferro and ferri-cyanides escapes precipitation (508–9).

Unoxidized ferrous iron (507) gives a dirty greenish pp of $Fe(OH)_2$, some remaining in solution, pp rapidly darkening and finally forming brown Fe_2O_3aq; but if partly oxidized to Fe''' a black pp of ferroso-ferric oxide ($Fe_3O_4 = FeO.Fe_2O_3$) forms, which is granular and easily washed.

Occasionally a faint pink color in filtrate indicates that some Cr has been retained in solution; this must be removed or tested for in pp IV.

515 If Fe has been completely removed in pp III a black pp on adding $(NH_4)_2S$ or H_2S indicates Ni or Co; any Fe not removed (see 507, 508) is ppd as black FeS.

516 Sometimes the ammonia pp (IV) is not filtered off before adding $(NH_4)_2S$, in this case the alternative method given in Table V must be followed, see also 277. One advantage of the intermediate filtration is that the absence of Ni and Co is indicated at once, and no time need be spent in attempting to separate them.

517 The ammonium sulphide used should be colorless or faintly yellow (140) and but little should be used. An excess not only dissolves NiS in presence of NH_4OH, but, especially if yellow, may deposit S on heating. Some prefer to pass gaseous H_2S through the ammoniacal solution; in this case care must be taken to keep it alkaline by addition of NH_4OHAq.

518 The ppd sulphides, especially NiS and CoS, readily oxidize when moist to soluble sulphates, and may be missed in the group separation, which should be carried on as soon as possible. H_2S prevents oxidation.

519 If filtrate is *brown* Ni is indicated; if so boil for some time to expel NH_3 (it is then best to nearly neutralize with HClAq and then make slightly acid with acetic acid and heat again); filter off the $NiS + S$ which falls and test in borax bead O.F. (oxidize well to get rid of S); it need not be added to main pp (IV).

520 $CaCO_3$ and $BaCO_3$ are *somewhat* soluble in NH_4ClAq. If a large excess of ammonium salts is present evaporate to dryness and ignite to expel them, dissolve residue in dilute HClAq, filter off any slight residue, add a little NH_4Cl and make alkaline with NH_4OH. If a white pp forms, filter, dry, and test with $Co(NO_3)_2Aq$ for Al or Mg.

521 Solution must be alkaline and NH_4Cl present to keep Mg in solution. If acid, CO_2 would be liberated on adding $(NH_4)_2CO_3$ and a soluble bicarbonate of Ca, etc., possibly formed.

The ammonium carbonate used should be free from bicarbonate (prepared by adding NH_4OH to a strong solution of the commercial salt).

522 Boiling may reconvert $CaCO_3 + 2NH_4Cl$ into soluble $CaCl_2$ and $(NH_4)_2CO_3$, or $NH_3 + CO_2$ which volatilize. (523.)

523 Whether $(NH_4)_2CO_3$ gives a pp or not, some Ba and Ca may be present in this solution, hence a few drops of ammonium sulphate and oxalate solutions should be added to remove them, pp may be subjected to flame test.

If a large amount of ammonium salt is present these traces of Ba and Ca are best removed after ignition and before testing for Mg (see separation of Mg, Na, and K, Table IV).

SILVER GROUP.

524 If silver group pp is large take a portion in test-tube, add 5 ccs water and boil, if entirely soluble it consists of $PbCl_2$ only; if not proceed as directed.

Lead must always be looked for in Copper group as well as here.

Traces of silver are likely to be missed, AgCl is slightly soluble in a solution of $PbCl_2$ as well as in other chlorides.

COPPER AND ARSENIC GROUPS.

525 The color of the pp thrown down by H_2S often indicates what metals are present, but the different sulphides may mask one another's colors.

If very large a *portion* of pp should be taken to test for As group; but before dividing it must be well mixed. It will often be noted that the colors of different portions differ greatly, the yellow As_2S_3 and CdS being among the last to fall.

526 CuS is slightly soluble in $(NH_4)_2SAq$ and HgS in $K_2S +$ KOHAq, hence it is generally preferable to use KOH or NaOH in presence of Cu (detected in the preliminary examination) and $(NH_4)_2S_x$ in presence of Hg; and it is well to test original solution for Cu by reducing with an iron wire and applying flame test to the deposit.

The $(NH_4)_2S$ should be slightly yellow, containing some polysulphide so as to convert insoluble SnS into soluble SnS_2: if too strongly yellow the S ppd on acidulation may entirely mask the actual group pp (test reagent with HCl before using): for the same reason as little of the reagent as possible should be used—too little rather than too much, as the As group (if it proves to be present in large proportion) can be separated completely by a second treatment.

CuS, if dissolved by $(NH_4)_2SAq$, is re-ppd with the As group sulphides of a brown or liver color, and may be neglected: black HgS sometimes falls from KOHAq. If Sn^{iv} and Hg occur together the Sn is incompletely separated from Hg by these means.

527 In very many places time will be saved by thus treating *portions* of heavy pps or bulky solutions, but it must be remembered that the amount of the substance to be tested for is proportionately reduced.

COPPER GROUP.

528 Any excess of acid has to be boiled off or neutralized later; the S obtained by the action of HNO_3 (see 140) is derived from the H_2S used as precipitant, not from the original substance.

529 A white substance found at this point may be $PbSO_4$ or $BaSO_4$ as well as $Hg_3S_2(NO_3)_2$, the latter dissolves in aqua regia like HgS. S is recognized by its burning readily when dried, leaving little or no residue: if plastic and present in large quantity it may inclose HgS or other sulphides: in such cases dry, burn, treat residue with HNO_3Aq filter and add filtrate to solution.

530 A small portion may be diluted and treated with a large excess of H_2S, if no pp or color is seen no metals need be looked for (see 525), provided too much acid were not used.

531 · The object of evaporating with H_2SO_4 is to expel the more volatile HNO_3 in which $PbSO_4$ is somewhat soluble.

532 The Bi pp must be carefully looked for and confirmed; if Pb is not completely removed it may fall here as white $Pb(OH)_2$ and Fe (from imperfect washing of Pp II or from reagents) as yellowish $Fe(OH)_3$. Sb, if not removed, may also pp here as white SbOCl, which is soluble in tartaric acid.

533 The test should be made with K_4FeCy_6 unless Cu has been otherwise *proved* to be present, the brown pp affords a more delicate test than the blue color of cuprammonium sulphate. A *blue* or greenish pp with K_4FeCy_6 shows that Fe has been imperfectly removed, or has been introduced in some way.

534 A black or brown pp shows that Pb or some other metal has not been completely separated, *e. g.*, Ni or Co owing to imperfect washing of Pp II.

ARSENIC GROUP.

535 If KOH or NaOH has been used for separation it is advisable to add some H_2S with the acid to insure complete precipitation.

536 Normal ammonium carbonate dissolves Sb sulphides slightly, in the acid carbonate that of As is alone soluble, solution is accompanied by escape of CO_2. Commercial ammonium carbonate yields a solution containing some acid carbonate (see 521), but less than NH_4HCO_3: a suitable reagent may be prepared by adding a little HClAq to a solution of the commercial carbonate so as to saturate it with CO_2.

537 If H_2S is not driven off by heat some Sb_2S_3 is reformed on dilution or cooling: but too long boiling may volatilize $SnCl_4$.

538 Some of the Sb passes off as SbH_3, especially if much free acid is present. Some Sn may be ppd on the platinum but always as a gray sponge. If a great deal of As is present some may be ppd at first, brown like Sb, but this is soon removed by the H as AsH_3. Cu gives a similar stain to that of Sb, which must be considered if $(NH_4)_2S_x$ is used and the As group pp appears brown.

539 If long boiled the $SnCl_2$ may oxidize to $SnCl_4$, which does not react and may be partly volatilized.

540 Pp may be dissolved in $HClAq + KClO_3$ and Marsh's test applied to it or to original solution: if dissolved in HNO_3Aq or aqua regia the test is less delicate. The AsH_3 (with possibly SbH_3) may be passed into $AgNO_3Aq$, AsH_3 giving a pp of Ag.

541 The method first given in the tables works well when As, Sb and Sn are not in too dissimilar proportions, but a very small amount of either may be missed in presence of a large amount of the others, and *absence* should be carefully confirmed.

IRON GROUPS.

542 If quite colorless contains no Fe, Mn, or Cr. If much Cr is indicated, and Zn has not been found, it is well to redissolve, pp Al, Fe and Cr as basic acetates, and test for Zn in the filtrate, as indicated under Pp IIIA.

543 Heating the KOHAq pps the $Cr(OH)_3$ which otherwise dissolves as $KCrO_2$.

544 NH_4Cl may also be used to pp Al (138): presence of Al may be confirmed by blue color after moistening pp with $Co(NO_3)_2Aq$, drying and *strongly* igniting. A little Al may come from reagents, especially KOH, or sometimes from vessels used.

545 CaF_2 will rarely be obtained here except from substances difficultly soluble in acids: if suspected test the *pp* also for Al by $Co(NO_3)_2Aq$, and for F by etching glass.

If $Si(OH)_4$ is suspected, dry pp and test in $NaPO_3$ bead, insoluble "skeleton" is SiO_2: TiO_2 acts similarly.

546 *At this stage* the Fe is in the ferric state, no matter what the original condition. If dissolved at the outset by the aid of HNO_3, aqua regia, etc., no information as to the state of oxidation can be gained from the solution: but the original color (see 406) may give some. If soluble in water or in HClAq, K_3FeCy_6 indicates Fe'' and KCNS Fe''', by blue and red colors with the original solution; but even this is not absolutely conclusive—*e. g.*, Fe_2O_3 mixed with a reducing agent or a sulphide dissolves in HClAq as $Fe''Cl_2$. If neither is found the Fe may be present as ferro- or ferricyanide, indicated by the effect of $FeCl_3$ and $FeSO_4$ on original solution. Many insoluble ferro- or ferricyanides give blue colors when evaporated with strong acids.

547 If blue or green test for Cr; if strongly yellow no further confirmation is necessary.

548 NiS and CoS are slightly soluble in dilute HClAq, but with difficulty even in the strong acid: presence of H_2S lessens the tendency to dissolve.

549 The actual separation of Ni and Co is tedious and requires great care, and is only necessary when they are present in very unequal proportions. Ni is often sufficiently indicated by the brown solution with $(NH_4)_2S$ (519) and Co by the blue borax bead. They may be separated after concentrating solutions (*a*) by making the acid solution alkaline with Na_2CO_3 then strongly acid with $HC_2H_3O_2$, and adding an excess of KNO_2 (solid or strong solution): this slowly oxidizes Co'' to Co''' and pps yellow $K_3Co'''(NO_2)_6$: Ni gives no pp unless some member of the Ca group is present, and may be tested for in the filtrate after allowing several hours for Co to pp.

(*b*) KCN is added to solution until pp formed just redissolves, solution is boiled five minutes, cooled, filtered if necessary, treated with a little KOH and then with BrAq in excess (keeping reaction alkaline with KOH): on standing in a warm place Ni pps as black $Ni(OH)_3$: Co remains dissolved as cobalticyanide $K_3Co'''Cy_6$. The pp and evaporated filtrate are tested in borax beads.

Co is sometimes lost by being ppd with Al and Cr: Ni by the use of an excess of $(NH_4)_2S$. Fe, if not removed, may be mistaken for Ni.

550 Mn is usually found in Pp III, and in that case need not be looked for here.

551 The Zn pp is easily overlooked, ZnS is the only white sulphide commonly ppd. An *excess* of H_2S may pp $Al(OH)_3$, converting the K into K_2S or KHS. This is avoided by first acidulating with acetic acid, which does not prevent precipitation of ZnS, but sometimes commercial acetic acid itself gives a slight white pp with H_2S.

552 Compare 516 and 277. The $BaCO_3$ method of separation is very satisfactory if sulphates are absent or removed by $BaCl_2$.

553 If Cr is present the Fe, Al and Cr are in this case best separated from Zn and Mn by the basic acetate method; Zn is ppd from the filtrate (containing free acetic acid) by H_2S, and Mn is then ppd on making it alkaline, and confirmed by fusing pp with Na_2CO_3.

554 Most of the Ni, Co and Zn was retained in solution by NH_4Cl, and if found in pp IV need not be further tested for.

555 The basic acetates of these triad metals redissolve, on cooling, in the free acid formed when they precipitate; they should be filtered as hot as possible.

556 Absence of H_3PO_4 here indicates that sufficient Fe (Cr or Al) was present originally to combine the whole of it; if present, more iron ($FeCl_3$) must be added.

557 The ppd phosphates are tested as the hydroxides, see pp 111.

558 It is advisable to insure removal of H_3PO_4.

559 It is well to evaporate and get rid of ammonium salts by ignition. Frequently enough of these metals will have escaped precipitation to allow of their being recognized in the examination of the groups in which they normally fall.

METALS OF ALKALIS AND ALKALINE EARTHS.

560 The amount of acetic acid should be adjusted to that of pp; by adding it in drops distributed over the filter paper a large excess is avoided.

561 The $K_2Cr_2O_7$ is added only in slight excess: $BaCrO_4$ is somewhat soluble in H_2CrO_4Aq.

562 In this group all the pps should be given ample time to form and settle.

563 Dilute H_2SO_4aq may be added to the solution (in acetic acid or HClAq) and a partial separation effected. The spectroscope is useful with Ca and Sr. The flame colors of the dominant metals are apt to mask those of metals present in small proportions, but often Ba, Ca and Sr may be detected in each other's presence by alternately dipping a platinum wire in solution, drying, and then holding for a minute or more in flame, trying the effect of different portions (*a*, *b*, *c*, fig. 11, page 35).

564 $BaSO_4$ gives scarcely any flame-color, but if heated on charcoal in R.F. it forms BaS, which is decomposed by HClAq and then reacts.

565 The amount of ammonium sulphate should be proportioned to that of the Ca and Sr present.

566 Some Ca may be carried down if either metal is present in large proportion, and some Sr may remain in solution with the Ca.

567 This is one of the most satisfactory methods of separation.

568 If no residue is left, Mg, Na and K are not present in appreciable quantities. Too high a temperature may volatilize KCl. Residue should be white, but usually brown flocks of insoluble matter (derived from dust) are seen on dissolving it.

569 The NH_4Cl is to prevent precipitation of Mg.

570 This pp must be given time (several hours may be necessary) to form; stirring or rubbing tube with a glass rod facilitates its formation, small crystals forming where tube is rubbed. Microcosmic salt may be used as a precipitant.

If Al (Ba or Ca) is present Na_2HPO_4 gives a flocculent non-crystalline pp; this should be treated with dilute acetic acid, which dissolves $MgNH_4PO_4$ but not $AlPO_4$, and the filtered solution re-ppd by NH_4OH. In presence of Cr and Fe much of the Mg may be lost by being carried down with them in Pp III (514).

571 The Na flame is rarely absent, but persistent only if Na is present in appreciable amounts. Wire must be thoroughly cleaned.

572 Rb and Cs give flame-colors resembling K, and some of the Li rays pass through blue glass. If either is suspected the spectroscope or H_2PtCl_6 should be used.

573 At this stage the ammonium salts introduced as reagents make it impossible to test.

574 Another method of separating Mg is (ammonium salts being expelled) to add $Ba(OH)_2Aq$ as long as a pp falls, filter off $Mg(OH)_2$, and remove the excess of Ba from filtrate by $(NH_4)_2CO_3$. This and the oxalate separation may be used quantitatively.

575 Li is ppd as phosphate by Na_2HPO_4 in alkaline solution. It may be separated from K and Na by the solubility of LiCl in amyl alcohol (fusel oil), the other chlorides being nearly insoluble.

The following books are recommended for study or reference in connection with the work of this course:

FRESENIUS: Manual of Qualitative Analysis* (Wiley & Sons).

PRESCOTT AND JOHNSON: Qualitative Analysis (Van Nostrand).

VALENTIN AND HODGKINSON: Qualitative Analysis (Churchill, London).

MUTER: A Short Manual of Analytical Chemistry (Simpkin & Marshall, London).

LANDAUER: Blowpipe Analysis* (Macmillan Co.).

BRUSH: Determinative Mineralogy and Blowpipe Analysis (Wiley & Sons).

OSTWALD: Foundations of Analytical Chemistry* (Macmillan Co.).

REMSEN: Inorganic Chemistry (Holt & Co.).

RICHTER: Inorganic Chemistry* (Blakiston & Co., Philadelphia).

ROSCOE AND SCHORLEMMER: Treatise on Chemistry (Inorganic), vol. i and ii (Appleton & Co.).

COMEY: Dictionary of Chemical Solubilities (Macmillan Co.).

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* Translation.

INDEX.

Numbers refer to paragraphs.

Acetates, 358.
Acids, 110–114.
Acid radicals, reactions, Part III.
  Examination for, 417–21.
Alkali- and alkaline earth metals, 279–92, 560–75, Table IV.
Alkalis, 329.
Alloys, 423.
Aluminium, 254–5.
Ammonium, 290.
Antimony, 232–7.
Aqua regia, 352.
Arsenic, 226–31.
  Group, 225–51, 525–7, 535–41, Table VI.

Barium, 281, 418.
Bases, 110, 115.
  Examination for, Tables III–VI.
Bismuth, 221–2.
Blowpipe tests, 143–9, 409–13.
Borates, 351.
Bromates, 355.
Bromides, 334.

Cadmium, 219–20.
Calcium, 283.
  Group, 280–3, 292, 560–7, Table IV.
Carbonates, 344.
Chlorates, 354.
Chlorides, 331–3.
Chromium, 256–9.
Citrates, 361.
Cobalt, 273–4.
Copper, 216–8.
  Group, 213–24, 525–34.
Cyanides, 339–41.
  Examination of, 419, 426.

Elements, lists of, 111, 113.
Equations, typical, 137–42.

Ferric salts, 261–2.
Ferrous salts, 267.
Ferro- and ferri- cyanides, 341.
Fluorides, 336.

Gases, 307–26.
Gold, 245.
  Ores, 427.
Groups of metals: alkalis, 286–92; arsenic, 225–51; calcium, 280–3, 292; copper, 213–24; iron, 252–77; silver, 203–12; Table I.
  Precipitation of, Table III, 502–23.

Humic acid, 362.
Hydroxides, 329
Hypochlorites, 356.

Insoluble substances, 422.
Iodates, 355.
Iodides, 335.
Iron, 260–2, 267.
  Group, 252–77, 542–59, Table V.

Laboratory work, 150.
Lead, 204–5, 215.
Lithium, 288.
Litmus reaction, 117, 414.

Magnesium, 284–5, 568–70.
Manganese, 268–70.
Marsh test, 227, 233.
Mercury, 208–10, 214.
Mercuric salts, 214.
Mercurous salts, 210.

Metallic radicals, reactions, Part II.
  Separations, 212, 224, 251, 277, 292, Part V.
  Examination for, Tables III to VI.
Metals, behavior, 293.
  Examination of, 423.
Molybdenum, 249.

Nickel, 271–2.
Nitrates, 352.
Nitrites, 353.
Nomenclature, 118–20.
Non-metals, behavior, 301–11.
  Compounds of, 312–28, 333.

Operations, 127–33.
Organic acids, 357.
Organic matter, interference, 357.
Ores, 427–8.
Oxalates, 359.
Oxidation and reduction, 122, 134.
Oxides, 329.

Permanganates, 270.
Phosphates, 348.
  In iron group pp, 262, 555–9, Table V.
Phosphites, 349.
Platinum, 246.
Potassium, 289.
Properties of substances, 103.

Rarer elements, 211, 223, 245–50, 263–5, 278, 291.
Reagents, 134–42.
Reactions, 123–6.

Salts, 110, 116.
Selenium, 248.
Separations, see Groups.
Silicates, 350, 422.
Silver, 206–7, 419.
  Group, 203–12, Table IV.
Simple substances, 402, Table II.
Solids, examination, 405–13.
  Solution of, 128, 405.
Stannic and stannous salts, 239–40.
Sodium, 287.
Strontium, 282.
Sulphates, 345.
Sulphides, 330.
Sulphites, 346.
Sulpho-, see Thio-.

Tartrates, 360.
Tellurium, 247.
Thiocyanates, 342.
Thiosulphates, 347.
Thio-salts, 120, 231, 237, 242–4.
Tin, 238–42.
Titanium, 264.
Tungsten, 278.

Uranium, 263.

Valence, 109.

Zinc, 275–6.

Page 44 –

1) $Pb(NO_3)_2 + 2HCl = PbCl_2 + 2HNO_3$

2) " " $H_2S = PbS +$ "

3) " " $H_2SO_4 = PbSO_4 +$ "

4) $2Pb(NO_3)_2 + 2KOH + H_2O = Pb_2O(OH)_2 + 2KNO_3 + 2HNO_3$
(Rem p 643)

5) $2Pb(NO_3)_2 + 2NH_4OH + H_2O = Pb_2O(OH)_2 + 2NH_4NO_3 + 2HNO_3$

6) $3Pb(NO_3)_2 + 2Na_2CO_3 + 2H_2O = Pb_3O_4(CO)_2(OH)_2 + 4NaNO_3 + 2HNO_3$
(Rem p 647)

7) $2Pb(NO_3)_2 + K_2Cr_2O_7 + H_2O = 2PbCrO_4 + 2HNO_3 + 2KNO_3$

8) $Pb(NO_3)_2 + 2KI = PbI_2 + 2KNO_3$

$3PbS + 8HNO_3 = 3Pb(NO_3)_2 + 2NO + 3S + H_2O$ (dil)

$3PbS + 8HNO_3 = 3PbSO_4 + 8NO + 4H_2O$ (conc)

Page 45 -

1- $AgNO_3 + HCl = AgCl + HNO_3$

2- $2AgNO_3 + H_2S = Ag_2S + HNO_3$

3- $2AgNO_3 + (NH_4)_2S = Ag_2S + 2NH_4NO_3$

4- $2AgNO_3 + 2KOH = Ag_2O + 2KNO_3 + H_2O$

5- $2AgNO_3 + 2NH_4HO = Ag_2O + 2NH_4NO_3 + H_2O$

6- $AgNO_3 + KCn = AgCn + KNO_3$

P-46-47.

1- $HgNO_3 + HCl = HgCl + HNO_3$

2- $2HgNO_3 + 2KOH = Hg_2O + 2KNO_3 + H_2O$

3- $2HgNO_3 + NH_4HO = Hg_2H_2N_2O_3 + HNO_3 + H_2O$

4- $2HgNO_3 + H_2S = Hg_2S + 2HNO_3$

5- $2HgNO_3 + (NH_4)_2S = Hg_2S + 2NH_4NO_3$

6- $4HgNO_3 + K_2Cr_2O_7 + H_2O = 2Hg_2CrO_4 + 2KNO_3 + 2HNO_3$

7- $2HgNO_3 + SnCl_2 = 2HgCl + Sn(NO_3)_2$

4
42.
7.

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